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Lecture Notes on Thermodynamics

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> *A theory is the more impressive the greater the simplicity of its premises is,*
> *the more different kinds of things it relates, and the more extended is its area of applicability.*
> *Therefore the deep impression which classical thermodynamics made upon me.*
> *It is the only physical theory of universal content concerning which I am convinced that,*
> *within the framework of the applicability of its basic concepts, it will never be overthrown.*
> Albert Einstein, 1949, *Notes for an Autobiography*

> *Thermodynamics is a funny subject.*
> *The first time you go through it, you don't understand it at all.*
> *The second time you go through it, you think you understand it, except for one or two points.*
> *The third time you go through it, you know you don't understand it,*
> *but by that time you are so used to the subject, it doesn't bother you anymore.*
> attributed to Arnold Sommerfeld, around 1940

Translation from French to English: Greg Cabailh[4]

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Preface and bibliography

Thermodynamics is a branch of physics that studies **macroscopic** systems (*i.e.* composed of a large number of particles) using an energetic approach. It is a theory that applies to many systems and allows to establish general relations between the coefficients that describe the various states of matter.

Statistical mechanics gives a **microscopic** interpretation to the quantities studied in thermodynamics. In simple cases, the postulates of statistical mechanics allow one to understand and interpret the laws of thermodynamics.

These lecture notes are intended for students who already have some notions in thermodynamics. After the first three chapters, which refer to key concepts (first and second laws, energy, entropy, work, heat, ...), more advanced notions of thermodynamics are discussed (potentials and thermodynamic functions, thermoelastic coefficients, phase diagrams, binary solutions, ...). Halfway through this course, two chapters outlining the fundamentals of statistical mechanics shed light on how the macroscopic properties of matter (as described by thermodynamics) are related to the microscopic behaviour of atoms and molecules; we will discuss (amongst other notions) the Boltzmann factor, the equipartition of energy, the statistical interpretation of entropy, the kinetic theory of gases, . . .

These notes are associated with about forty short videos explaining the most tricky and important points of this course.

Short bibliography

- Jancovici, *Statistical physics and thermodynamics*, Wiley (1973)
  A concise book, ideal to review the basics of thermodynamics. It also addresses statistical mechanics.
- Kubo, *Thermodynamics: an advanced course with problems and solutions*, North Holland (1968)
  Reference book with many examples and problems with complete solutions.
- Landau and Lifshitz *Statistical Physics*, Elsevier, (1980)
  More difficult (advised as a second reading): A classic, timeless, extremely concise!
- Callen *Thermodynamics and an introduction to thermostatistics*, Wiley (1985)
  A very formal book, the reading of which is strongly recommended.
- Reif *Berkeley Physics Course, Vol. 5: Statistical Physics*, Mc Graw-Hill Dunod (1967)
  Another classic, detailed, with illustrations, that you will enjoy reading!
- Reif *Fundamentals of statistical and thermal physics*, Waveland Press (2009)
  Book by the same author as the previous one, more advanced and swift in its presentation.

Chapter 1

Video 1

Review of basic concepts

1.1 Thermodynamic systems

Video 2

Thermodynamics is the science of macroscopic systems, *i.e.* of systems composed of N particles (atoms, molecules, ions, *etc.*), N being very large ($N \gg 1$).

Video 3

Frame 1.1 : **Orders of magnitude**

Under normal conditions, the typical distance between particles is approximately:
- $3\,\text{Å} = 0.3\,\text{nm} = 3\,10^{-10}\,\text{m}$ for solids or liquids,
- $3\,\text{nm}$ for gases.

In 1 cm^3 of matter, there are typically between:
- 10^{22} to 10^{23} particles for solids or liquids,
- 10^{19} to 10^{20} particles for gases.

Recall that a mole is defined as the amount of substance in 12 g of carbon 12 and the Avogadro constant $\mathcal{N}_A$ gives the number of particles per mole:

$$\mathcal{N}_A = 6.022\,10^{23}\,\text{mol}^{-1}.$$

Only a few cm^3 to a few tens of cm^3 of solid or liquid are required to obtain a mole. For an ideal gas, at atmospheric pressure and a temperature of 0°C, the volume of a mole is $22.4\,\ell$.

Thermodynamics studies the properties of matter at a macroscopic level, *i.e.* with a number of particles so large that it is not feasible to study each individual trajectory.

Frame 1.2 : **Thermodynamic systems**

A thermodynamic system is the object of the study under review. What is not in the system is defined as the surroundings. A system can be:
- open or closed, depending on whether it can exchange matter, or not, with its surroundings,
- non-isolated or isolated, depending on whether it can exchange energy, or not, with its surroundings,
- movable or rigid.

Remark: if the system is open, it cannot be isolated.

1.2 Thermodynamic equilibrium

If a system is left standing for a sufficiently long time, it will reach a state of thermodynamic equilibrium.

Frame 1.3 : **Thermodynamic equilibrium**

A system is considered under thermodynamic equilibrium when there is no more macroscopic movement nor any kind of flux.

!

- When a system is in equilibrium, there is no macroscopic movement (we cannot see anything moving) but, considered individually, particles move randomly with high velocity.
- A conducting wire in which flows an electric current is not in equilibrium since there is a flux of charges as well as thermal dissipation.
- A piece of metal connecting a hot source to a cold source is not in equilibrium since there is heat transfer and hence an exchange of energy from the hot towards the cold source.

1.3 Thermodynamic variables

At thermodynamic equilibrium, it is sufficient to know a small number of quantities to fully characterise a system. These quantities are called thermodynamic variables.

Frame 1.4 : **Thermodynamic variables**

Thermodynamic variables are the quantities used to characterise a system.

- Some variables have a meaning even when the number of particles in the system is small. Such variables are derived from geometry, mechanics, electromagnetism, *etc.*; *e.g.* volume V, surface $\mathcal{S}$, number of particles N, amount of substance n (in moles), applied force, internal energy U, magnetisation $\mathcal{M}$, *etc.*
- Other variables only have a meaning for systems with a large number of particles; *e.g.* gas pressure p, temperature T, chemical potential μ, entropy S, *etc.*

A thermodynamic variable is said to be *extensive* if it is proportional to the amount of substance in the system, and *intensive* if it is independent. A thermodynamic variable is *additive* if the value associated with a system composed of several parts is equal to the sum of the values associated with each individual part.

Example 1: A glass of $10\,c\ell$ is taken from a bathtub filled with $100\,\ell$ of water. In the glass, there is a thousand times less particles, moles, volume, energy, entropy than in the bathtub; these quantities are extensive. On the other hand, the temperature, pressure and chemical potential of the water are the same in the bathtub and in the glass; these quantities are intensive. The contact surface between water and air has a complicated dependence on the geometry of the glass and the bathtub; this surface is a quantity that is neither intensive nor extensive.

Example 2: The system considered is the content of a half filled bottle, *i.e.* a liquid (bottom part) and a gas (top part). The energy of the system is equal to the energy of the liquid plus the energy of the gas; this quantity is additive. It is also the case for volume, entropy, *etc.*

Remark: In general, additive and extensive variables are the same.

Some variables are easy to measure (volume, temperature, pressure in a fluid, *etc.*) and others can only be obtained through a calculation (internal energy, entropy, chemical potential, *etc.*). We distinguish external and internal variables.

- *External* variables are those controlled by the operator, either by maintaining them fixed (*e.g.* mass m of a closed system, volume V of a rigid system), or by exerting an action on the system (*e.g.* pressure of a pressostat p_0, temperature of a thermostat T_0).
- The variable is *internal* (or free) when the operator does not have direct access to it (even if he can define it or measure it). For example, this is the case of the number of reagent particles in a closed system in which a chemical reaction occurs. The value of these variables is fixed only by the thermodynamic equilibrium conditions.

For a pure single phase fluid, the equilibrium state of the system is entirely determined by three thermodynamic variables, for example n, V and T or n, V and $U\ldots$ The values of the other variables can then be obtained using the equation of state (relationship between p, n, V and T) and other relationships, see the example of the ideal gas in frame 1.5, or of the van der Waals gas in frame 1.10.

Frame 1.5 : The ideal gas

The ideal gas is an ideal thermodynamic system where the interactions between particles are neglected. For a classical ideal gas (where quantum effects are neglected), the equation of state (ideal gas law) is

$$pV = nRT$$

p: pressure (Pa)
n: amount of substance (mol)
V: volume (m^3)
T: temperature (K)

where $R = 8{,}31\,\mathrm{J/K/mol}$ is the ideal gas constant. We can also write

$$pV = Nk_BT$$

N: number of particles

where $k_B = 1{,}38\,10^{-23}\,\mathrm{J/K}$ is the Boltzmann constant. Since $N = n\mathcal{N}_A$, we have

$$R = \mathcal{N}_A k_B.$$

When the ideal gas is monoatomic, we also have the relationship

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_BT$$

U: internal energy (J)

The ideal gas is a very good approximation of the usual real gases at ordinary temperatures and pressures. However, when the molar density n/V becomes high, the ideal gas approximation is no longer satisfactory: the mean distance between particles decreases and the interaction potential between them makes for a sizeable contribution to the total energy of the gas. On can then use a better approximation such as the van der Waals gas, see frame 1.10.

Video 4

1.4 Transformations

In thermodynamics, one is interested in the transformations of a system and most often in transformations between two equilibrium states. Let us consider a system transiting between two equilibrium states (i) to (f) and X a state variable passing from the value X_i to X_f, *e.g.* the temperature T which would change from $T_\mathrm{i} = 20\,°\mathrm{C}$ to $T_\mathrm{i} = 60\,°\mathrm{C}$. The variation of X during the transformation is defined by $\Delta X = X_\mathrm{f} - X_\mathrm{i}$, *i.e.* $\Delta T = T_\mathrm{f} - T_\mathrm{i} = 40\,°\mathrm{C}$ in our example. By definition, this variation only depends on the initial and final states and not on the sequence of intermediate states. In short, ΔX does not depend on the path of the process followed.

Some transformations are brutal which can lead to intermediate states being poorly defined: this is the case of a gas expansion in vacuum or an explosive chemical reaction. In thermodynamics, we are more often interested in slower transformations for which the state of the system is well defined at each moment. In particular, *quasistatic* transformations and *reversible* transformations are of crucial importance:

Frame 1.6 : Quasistatic transformation

A transformation is said to be *quasistatic* when it evolves slowly enough for the system to be described by a continuous succession of (internal) equilibrium states. During a quasistatic transformation, all the state variables X_1, X_2, … of the system are defined and vary continuously. We can then express the differential of any state function $\mathit{\Phi}(\{X_n\})$ as

$$\mathrm{d}\mathit{\Phi} = \sum_n \left.\frac{\partial \mathit{\Phi}}{\partial X_n}\right|_{X_{m\neq n}} \mathrm{d}X_n = \sum_n Y_n\,\mathrm{d}X_n, \quad \text{with} \quad Y_n = \frac{\partial \mathit{\Phi}}{\partial X_n},$$

as well as the variation

$$\Delta\mathit{\Phi} = \mathit{\Phi}_\mathrm{f} - \mathit{\Phi}_\mathrm{i} = \int_\mathrm{i}^\mathrm{f} \mathrm{d}\mathit{\Phi}.$$

The fact that $\Delta\mathit{\Phi}$ does not depend on the path followed is ensured by the fact that $\mathrm{d}\mathit{\Phi}$ is the differential of a state function. In mathematics, we can show that the expression of $\mathrm{d}\mathit{\Phi}$ is a differential if, and only if, all the following relations are verified

$$\frac{\partial Y_n}{\partial X_m} = \frac{\partial Y_m}{\partial X_n}$$

(cross partial derivatives equality, Schwarz's theorem). The application of these relations to a state function $\mathit{\Phi}$ constitutes Maxwell's relations in thermodynamics. We will return to this in chapter 4.

Frame 1.7 : Reversible transformation

A transformation is said to be *reversible* when the path of the process can be followed, in the same external environment, by reversing the direction of time (in other words, the transformation obtained by reversing the procedure is credible). Conversely, a transformation that is only feasible in the normal direction of time is described as *irreversible*.

For a transformation to be reversible, it is necessary to control step by step the evolution of the system, which means that all the state variables must be permanently constrained by the operator (*i.e.*, they do not vary without the control of the operator). For such an occurrence, not only does the system follow a quasistatic transformation, but it is also permanently in equilibrium with its surroundings.

The concepts of quasistatic and reversible transformations are close, but distinct:

quasistatic transformation $\iff$ succession of equilibrium states of the system,
reversible transformation $\iff$ succession of equilibrium states of the universe.

Any reversible transformation is therefore quasistatic, however the reciprocal is generally false (but nevertheless true in a large number of cases).

The following terms are used for thermodynamic transformations:

isobaric $\iff$ the pressure p of the system is constant,
monobaric $\iff$ the external pressure p_0 is constant,
isochoric $\iff$ the volume V of the system is constant,
isotherm $\iff$ the temperature T of the system is constant,
monotherm $\iff$ the outside temperature T_0 is constant,
adiabatic $\iff$ the system evolves without heat exchange with its surroundings.

1.5 Internal energy U

Video 5

The energy of a system E_{tot} can be divided in two, the macroscopic energy and the microscopic energy or *internal energy* U.

- The macroscopic energy includes the overall motion of a system (solid in rotation, flow in a fluid, *etc.*), potential energies (electrostatic energy if the system is charged, potential energy of gravity, *etc.*), and so on.
- The internal energy represents the rest of the energy of the system: molecular motion, energy of interaction between particles, *etc.*

In thermodynamics, one almost always considers situations where the macroscopic energy is constant: the system is immobile (macroscopically), does not change altitude, *etc.* The energy variations of the system are then equal to the variations of the internal energy:

$$\Delta E_{\text{tot}} = \Delta U \qquad \text{(in most cases).} \tag{1.1}$$

The internal energy is defined as the sum of several terms:

Frame 1.8 : Different types of internal energies

Translational kinetic energy $E_{\mathbf{trans}}$ is the kinetic energy accounting for the motion of the particles. For a classical system at rest, it is written as

$$E_{\text{trans}} = \sum_{i=1}^{N} \frac{1}{2} m_i \mathbf{v}_i^2$$

the sum is over the N particles of the system
m_i: mass of the particle i,
$\mathbf{v}_i$: velocity (vector) of the center of mass of particle i

(it is more complicated for a quantum system...)

Interaction energy between particles $E_{\mathbf{int}}$ which can be written as

$$E_{\text{int}} = \sum_{(i,j)} u(r_{i,j})$$

the sum is over all pairs of particles; hence there are $\frac{N(N-1)}{2}$ terms
$r_{i,j}$: distance between particules i et j
u: interaction potentiel.

(see frame 1.9 for more details on the interaction potential $u(r)$.)

Rotational kinetic energy $E_{\mathbf{rot}}$ which represents the kinetic energy due to the rotation of the particles on themselves.

Vibrational kinetic energy $E_{\mathbf{vib}}$ which represents the kinetic and elastic energy due to the internal vibrations of the particles.

Other energy terms may contribute depending on the application, *e.g.* the energy in the excitations of the electronic cloud (at high temperature), the interaction energy with the magnetic field, *etc.*

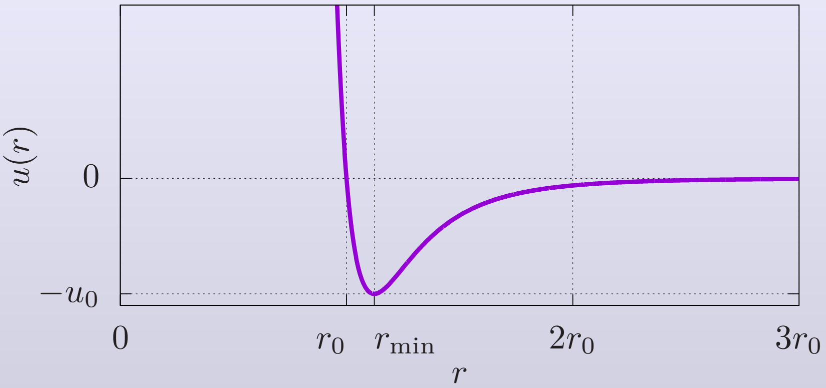
The internal energy is the sum of all these terms:

$$U = E_{\text{trans}} + E_{\text{int}} + E_{\text{rot}} + E_{\text{vib}} + \cdots$$

The interaction energy E_{int} is important in liquids and solids, but is weak (and often negligible) in gases. By definition, it is zero for the ideal gas.

Frame 1.9 : The interaction potential

The interaction potential $u(r)$ between two particles separated by a distance r (refer to frame 1.8 for the definition of E_{int}) often has the form displayed hereafter:



- r_{min} is the distance for which the energy is minimal: the interaction is repulsive for $r < r_{\text{min}}$ and attractive for $r > r_{\text{min}}$.
- The repulsive force is extremely strong for $r < r_0$ so that the distance between

two particles is almost always greater than r_0.
- Both distances r_{min} and r_0 are typically of the order of a few Ångströms.
- When r is large, the decrease in potential is very fast: it has a $1/r^6$ dependency. (This force originates from the dipole-dipole interaction between atoms, also called the van der Waals force. It is an electrostatic force.) Usually, the interaction between two particles becomes negligible when their distance is greater than approximately three times r_0, *i.e.* typically one nanometer.

Taking into account this interaction potential leads, as a first approximation, to the van der Waals gas, see frame 1.10.

Frame 1.10 : The van der Waals gas

When matter density increases and the ideal gas approximation is no longer satisfactory, one needs to take into account the interaction potential described in frame 1.9. The main two effects are the following:

- Because of the repulsive part of the potential, the volume that the gas can occupy is effectively smaller by an amount which is proportional to the number of particles.
- Because of the attractive part of the potential, the particles heading towards the boundaries are slowed down by the rest of the gas; one shows that this has the effect of reducing the pressure by an amount proportional to the square of the matter density.

To take these two effects into account, van der Waals wrote in 1873 an equation of state which reads

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT,$$

where a and b are two gas dependent constants. As opposed to the ideal gas equation, the van der Waals gas equation is gas-dependent. This quite simple equation allows to understand a large number of observations, including the liquid-gas phase transition. In this approximation, the internal energy of a monoatomic gas can be written

$$U = \frac{3}{2} nRT - a\frac{n^2}{V}$$

In all the situations we will encounter in this course, the internal energy will be an additive quantity. This means that if a system is composed of two parts A and B, we can define U_A (or U_B) as the energy that system A (or system B) would have if considered separately (alone), and U_{A+B} as the energy of the entire system, therefore

$$U_{A+B} = U_A + U_B. \tag{1.2}$$

To understand this result, the internal energy can be broken down as explained in frame 1.8: $U = E_{\text{trans}} + E_{\text{int}} + E_{\text{rot}} + E_{\text{vib}} + \cdots$. The terms E_{trans}, E_{tot}, E_{vib}, *etc.* are clearly additive terms. The only problematic term is the interaction energy E_{int}. This interaction energy is usually written as a sum over all pairs of particles (i, j) of the interaction potential u between these two particles. In this sum there are three types of terms: the terms where both particles are in part A, the terms where both are in B, and the terms where one particle is in A and the other in B:

$$E_{\mathrm{int},A+B} = \sum_{(i,j)} u(r_{i,j}) = \sum_{\substack{(i,j)\\ i\in A, j\in A}} u(r_{i,j}) + \sum_{\substack{(i,j)\\ i\in B, j\in B}} u(r_{i,j}) + \sum_{\substack{(i,j)\\ i\in A, j\in B}} u(r_{i,j}). \tag{1.3}$$

(Recall that $r_{i,j}$ is the distance between particles i and j.) The first term on the right-hand side is $E_{\mathrm{int},A}$, the interaction energy of part A. Similarly, the second term is $E_{\mathrm{int},B}$. The third term is usually negligible. Indeed, assuming that the interaction potential $u(r)$ is similar to the one described in frame 1.9, then the only pairs of particles (i, j) with $i \in A, j \in B$ for which $u(r_{i,j})$ is not negligible are those which are on either side of the border between A and B, in a layer of the order of the nanometer. This third term therefore concerns very few particles with respect to the first two and is considered negligible. Hence we find that E_{int} is an additive quantity and, therefore, the internal energy U is also, as expressed earlier. However, there are two types of situations (which we will not consider in this course) where the internal energy is no longer additive:

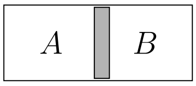
- When the dimensions of the system are of the same order of magnitude as the interaction length *i.e.* of the order of the nanometer. (But in this case are we still doing thermodynamics?)
- When the interaction potential is not similar to the one described in frame 1.9 and decreases slowly with distance (long range force). This is the case for example if the system has a non-zero electrical charge (the electrostatic potential decreases in $1/r$ only), or if we study the thermodynamics of a galaxy: the interaction between two particles (*i.e.* between two stars) is gravitational and has a potential that decreases in $1/r$.

1.6 Pressure p

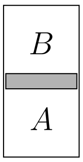
A fluid exerts on a surface element $\mathrm{d}\mathcal{S}$ of a wall a *force of pressure* perpendicular to $\mathrm{d}\mathcal{S}$, directed outwards with a norm equal to $p\,\mathrm{d}\mathcal{S}$, where by definition p is the *pressure* of the fluid.

> ! The force of pressure, which is a force, a vector quantity the SI unit of which is the Newton, should not be confused with the pressure, a scalar quantity whose SI unit is the Pascal.

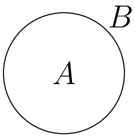
At thermodynamic equilibrium, the system must specifically be at mechanical equilibrium. Let us consider three examples:



Two fluids A and B are separated by a partition which can slide horizontally. Mechanical equilibrium imposes $p_A = p_B$.



Two fluids A and B are separated by a partition which can slide vertically. Mechanical equilibrium imposes $p_A = p_B + \frac{Mg}{\mathcal{S}}$, with M the mass of the moving wall, $\mathcal{S}$ its surface and g the gravitational acceleration.



The fluid A is enclosed in an elastic membrane (balloon, soap bubble, *etc.*) which is immersed in the fluid B (typically the atmosphere). Then $p_A > p_B$, and the difference between the two pressures depends on the elastic properties of the membrane and its radius of curvature.

> ! If the partition between A and B is not mobile, this means that something is keeping it motionless regardless of the pressures exerted by A and B. In particular we can have $p_A \neq p_B$.

From a microscopic point of view, the pressure can be understood as the effect of the particles hitting the walls. A calculation, as detailed in the video, gives for a classical ideal gas consisting of N identical particles:

Video 6

Video 7

$$p = \frac{1}{3} m \frac{N}{V} v_q^2. \tag{1.4}$$

p: pressure (Pa) m: mass of a particle (kg)
N: number of particles V: volume (m^3)
v_q: root-mean-square speed (m/s)

The root-mean-square speed v_q is an estimate of the typical velocity of a particle. Its precise definition is

$$v_q = \sqrt{\frac{1}{N}\sum_{i=1}^{N} \mathbf{v}_i^2} = \sqrt{\langle \mathbf{v}^2 \rangle}, \tag{1.5}$$

the sum is over the N particles of the system
$\mathbf{v}_i$: velocity (vector) of the particle i.

(The notation $\langle \mathbf{v}^2 \rangle$ can be read as the mean value of $\mathbf{v}^2$ and is by definition $\frac{1}{N}\sum_i \mathbf{v}_i^2$.) The translational kinetic energy can be written as $E_{\text{trans}} = N \times \frac{1}{2} m v_q^2$ (see frame 1.8 and (1.5)). We can deduce that for any ideal gas, we have

$$pV = \frac{2}{3} E_{\text{trans}} \tag{1.6}$$

For all ideal gases
p: pressure (Pa) V: volume (m^3)
E_{trans}: translational kinetic energy (J)

For an ideal monoatomic gas, we have $U = E_{\text{trans}}$ and therefore

$$pV = \frac{2}{3} U \tag{1.7}$$

For an ideal monoatomic gas
U: internal energy (J)

By using the ideal gas law $pV = nRT$, we obtain

$$E_{\text{trans}} = \frac{3}{2} nRT \quad \text{(for all classical ideal gases)}, \tag{1.8}$$

and obviously $U = \frac{3}{2} nRT$ for a classical monoatomic ideal gas.

1.7 Temperature T

The temperature of a thermodynamic system is a quantity that must verify the following property:

> When two systems A et B with different temperatures T_A and T_B are brought into contact, the energy (in the form of heat) flows spontaneously from the body having the highest temperature to the body having the lowest one.

This property is however not sufficient to clearly define temperature. There are several ways to define the latter:

With a temperature scale. If the temperature of a given system is known, the temperature of all other systems can be deduced by comparison. For example, we can define the temperature of an ideal gas by

$$T = \frac{pV}{nR}. \tag{1.9}$$

(See frame 1.5.) The temperature of any system can then be defined as the temperature of the ideal gas with which it is in thermal equilibrium.

The problem with this definition is that the ideal gas is theoretical, and real gases can only be approximated to an ideal gas.

From the microscopic thermal motion. In a classical ideal gas, there is a simple relation (1.8) between the translational kinetic energy and the temperature:

$$E_{\text{trans}} = \frac{3}{2} nRT. \tag{1.10}$$

This relation remains valid for any classical system (*i.e.* for any system where the quantum and relativistic effects can be neglected) and can therefore be used as a definition of temperature. From this point of view, temperature is a direct measurement of molecular thermal motion. By introducing the mean translational kinetic energy per particle $\epsilon_{\text{trans}} = E_{\text{trans}}/N = \frac{1}{2} m v_q^2$ and recalling that $nR = Nk_B$, we can also write for a particle:

$$\epsilon_{\text{trans}} = \frac{3}{2} k_B T. \tag{1.11}$$

This definition works for gases, liquids and solids at usual temperatures. However, it does not work for systems where quantum effects are strong. If we tried to determine the temperature of the conduction electrons in a metal at room temperature using (1.11), we would find a temperature between 10^4 et 10^5 Kelvin!

By derivation of the entropy. In an abstract manner, the temperature in defined by

$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{n,V,\ldots}. \tag{1.12}$$

Although very abstract, this definition is valid in all situations. It is the most accurate way to define the temperature.

Chapter 2

Video 1

Energy transfer

2.1 Energy conservation, work, heat

A system undergoing a transformation from a state A to a state B is considered. Assuming that the system is macroscopically at rest in states A and B, energy conservation gives:

$$\Delta U = U_B - U_A = [\text{energy received by the system between } A \text{ and } B].$$

Remark: The energy received is an algebraic quantity. If the energy received ΔU is positive, the system receives energy. If the energy received ΔU is negative, the system gives away energy.

Energy gains are classified into two categories, the work received W and the heat received Q:

Frame 2.1 : **First law**

During a transformation, we have

$$\Delta U = W + Q$$

U: internal energy
W: work received
Q: heat received

(The three quantities W, Q and ΔU can be positive, negative or zero).

- The work received W corresponds to the macroscopic energy exchanges; it should be possible to determine it by measuring the various forces applied to the system. A work received W occurs with the change of a macroscopic parameter of the system other than energy. For example, the work of pressure forces comes with a change in volume, the work of magnetic forces comes with a change of magnetisation, *etc.*
- The heat received Q corresponds to the spontaneous energy exchanges between two bodies at different temperatures, either by contact (conduction), or at a distance (radiation), or by means of a moving fluid (convection). These energy transfers occur at the microscopic level and are sometimes difficult to determine with precision.

For an infinitesimally small transformation, we write

$$\mathrm{d}U = \delta W + \delta Q \quad \text{with } \Delta U = \int_A^B \mathrm{d}U, \quad W = \int_A^B \delta W \quad \text{and } Q = \int_A^B \delta Q.$$

- U is a state function, a property of the system. $\Delta U = U_B - U_A$ is the difference in U between two different states A and B and $\mathrm{d}U$ is the difference (infinitesimal) between two infinitely close states. The quantity ΔU depends only on the states A and B and does not depend on the intermediate states.
- W and Q are two properties of the transformation. They depend on A, B and all intermediate states (*i.e.* the transformation path followed). They cannot be expressed as the difference of a quantity taken in B and A. Similarly, δW and δQ are infinitesimal energy gains during a transformation between two infinitely close states. They do not correspond to a difference.

Remark: Transformations without heat or work exchange are possible. The typical example is the Joule expansion (described in more detail in section 3.1.1): a gas is in an adiabatic enclosure; a tap is opened which allows the gas to flow into another adiabatic enclosure previously under vacuum. During the transformation the gas receives neither heat (all the walls are adiabatic) nor work (there is no external force). Therefore we have $Q = 0$, $W = 0$ and, of course, $\Delta U = 0$. If the gas is ideal, since U does not depend on V, it implies that $\Delta T = 0$. If the gas is real, U is an increasing function of T and V (see, for example, the expression of U for a van der Waals gas, frame 1.10), and $\Delta U = 0$ implies $\Delta T < 0$.

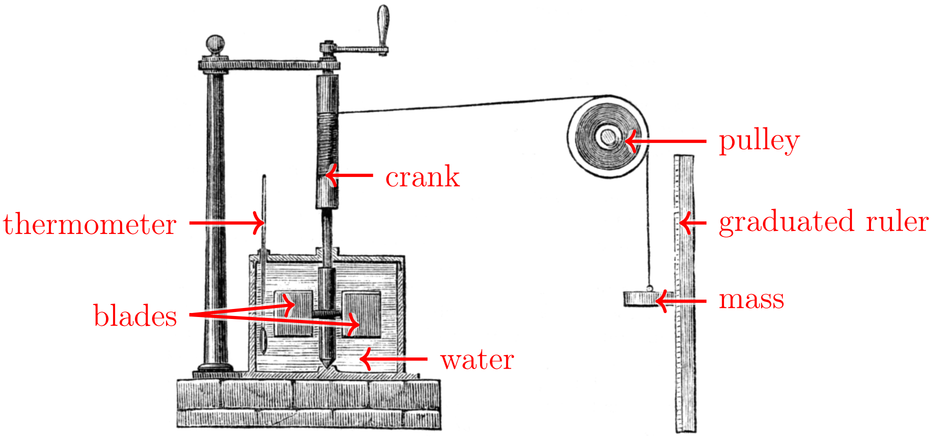


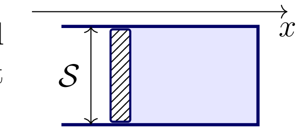
Figure 2.1: The Joule apparatus to establish heat/energy equivalence.

The historical content of the first law is that heat, considered until the mid-nineteenth century as a separate quantity (with its own unit, the calorie), is actually a form of energy (expressed in joules) similar to mechanical energy. The historical experience of Joule in 1845, see Figure 2.1, made it possible to highlight the heat/energy equivalence: a mass m which falls from a height H drives the rotation of blades in a volume of thermally insulated water. Once all macroscopic movements in the water have stopped, a thermometer indicates a temperature increase. The same result could have been obtained by supplying the system with heat (in calories) equal to the mass of water (in grams) multiplied by the temperature variation (in Celsius). Instead a mechanical energy equal to mgH (potential energy of gravity) was supplied. Heat is therefore a form of energy and calorie can be expressed in joules. (Reminder: $1\,\mathrm{cal} = 4.186\,\mathrm{J}$.)

2.2 Some examples of energy exchange through work

Video 2

2.2.1 Work of pressure forces



A system whose volume is likely to change is considered. A typical example is a gas in a container closed by a piston, as in the adjacent figure.

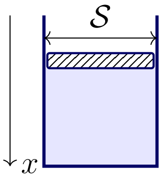
The system considered here is the whole system {gas+piston}. The external force exerted on this system is the pressure force due to the surroundings (typically: the atmosphere). By labelling the external pressure p_{ext}, the force is directed in the increasing x-direction with its norm equal to $\mathcal{S}p_{\text{ext}}$, with $\mathcal{S}$ the surface of the piston. When the piston position increases by $\mathrm{d}x$, the work of the pressure force, which is also the work received by the system is

$$\delta W = p_{\text{ext}}\mathcal{S}\,\mathrm{d}x = -p_{\text{ext}}\,\mathrm{d}V,$$

where $\mathrm{d}V = -\mathcal{S}\,\mathrm{d}x$ is the volume variation of the system.

Remarks:

- The expression $\delta W = -p_{\text{ext}}\,\mathrm{d}V$ is valid for all geometries, not just for a piston. For example, this expression applies to a balloon that is inflated, a metal that expands, *etc.*
- If the piston slides vertically and its mass M is not negligible (or if a mass M is placed on it), the weight also contributes some work. Usually, the work of the weight is included in the work of the pressure forces and one still writes $\delta W = -p_{\text{ext}}\,\mathrm{d}V$, but where $p_{\text{ext}} =$ (the real external pressure) $+\frac{Mg}{\mathcal{S}}$. See also section 1.6.



- When a transformation is slow enough so that the system is permanently under mechanical equilibrium (this is the case for a reversible transformation), we always have $p = p_{\text{ext}}$ (with p the fluid pressure) and thus $\delta W = -p\,\mathrm{d}V$.
- For a violent transformation, it may happen that p is not defined or that $p \neq p_{\text{ext}}$. It is then necessary to be cautious, in the energy balance, to the fact that the piston (which is part of the system!) gains a macroscopic kinetic energy. We must therefore write $\mathrm{d}E_{\text{total}} = \delta W + \delta Q$, and not $\mathrm{d}U = \delta W + \delta Q$. If at the end of the transformation the piston is at rest, one may have to wonder whether it has returned its kinetic energy to the gas in the container or to the surroundings.

For a transformation where the external pressure is constant, we have of course $W = -p_{\text{ext}}\,\Delta V = -\Delta(p_{\text{ext}}V)$. When the external pressure is constant and the system is in mechanical equilibrium at the initial ($p_{\text{ext}} = p_{\text{initial}}$) and final ($p_{\text{ext}} = p_{\text{final}}$) stages, the work of the pressure forces is then $W = -\Delta(pV)$ and, if there are no other forces producing work,

$$\Delta H = Q \qquad \text{if } p_{\text{ext}} \text{ constant and } p_{\text{initial}} = p_{\text{final}} = p_{\text{ext}}, \tag{2.1}$$

where the enthalpy H is defined by

$$H = U + pV.$$

(See also frame 4.3.) Expression (2.1), valid for a “transformation at constant pressure”, is to be compared to the expression $\Delta U = Q$ valid when $W = 0$, *i.e.* for a “transformation at constant volume”.

2.2.2 Elastic work

If we pull on an elastic band with a force of norm f_{ext}, the system receives work

$$\delta W = f_{\text{ext}}\,\mathrm{d}L,$$

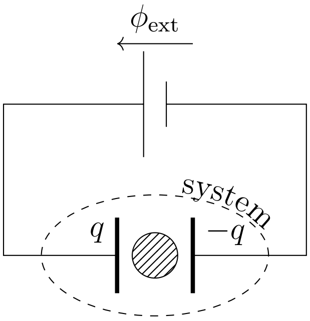
where $\mathrm{d}L$ is the length increase of the band during the transformation.

The remarks made for the work of pressure forces can also be made here:

- When the transformation is slow enough so that we can consider that there is permanent mechanical equilibrium (this is the case, for example, of a reversible transformation), we have at any moment $f = f_{\text{ext}}$ with f the tension of the band and thus $\delta W = f\,\mathrm{d}L$.
- For a violent transformation (for example, we stretch the rubber band and then let go of one end), we must take into account the macroscopic kinetic energy in any energy balance.

To study this kind of systems, we sometimes define an enthalpy $H = U - fL$. We then have $\Delta H = Q$ for a transformation at constant tension without any other source of work.

2.2.3 Electric work



A system made of a sample placed between the armatures of a capacitor is considered. A voltage ϕ_{ext} is applied to this capacitor by a generator; it is this generator (placed outside the system) that delivers the work. During a transformation that, for example, changes the capacity of the capacitor, the electric charge on its plates changes. The work received is then

$$\delta W = \phi_{\text{ext}}\,\mathrm{d}q,$$

where q is the charge of the plate connected to the + terminal of the generator.

2.2.4 Chemical work

When the system is open, it can exchange substance with the surroundings and the number of moles n can vary.

As a first example, imagine a closed recipient containing water in vapour and liquid forms (for example a pressure cooker the valves of which are in the closed position). By heating the recipient, the system “water vapour in the recipient” will see its amount of substance increase: water will pass from the liquid to the vapour phase. If n_{v} denotes the amount of water in the vapour phase, the system receives an energy proportional to $\mathrm{d}n_{\text{v}}$ during an infinitesimal transformation $n_{\text{v}} \to n_{\text{v}} + \mathrm{d}n_{\text{v}}$. It is the *chemical work*:

$$\delta W = \mu_{\text{ext}}\,\mathrm{d}n_{\text{v}}, \tag{2.2}$$

where μ_{ext} depends on the properties of the surroundings, here the liquid. μ_{ext} is called the chemical potential. We will return in several chapters to this very important quantity.

The generalisation to mixtures of different species is immediate. Imagine that the system contains different chemical species with a number of moles n_i for each (i is the index of the different species). To simplify, we will assume that there is only one phase. During an infinitesimal transformation of the amount of substance of each species (for example, during a chemical reaction), the infinitesimal work is given by

$$\delta W = \sum_i \mu_{\text{ext}}^{(i)}\, \mathrm{d}n_i. \tag{2.3}$$

2.3 Some examples of heat exchange

Video 3

2.3.1 Heat exchange by contact (conduction)

If a body X at temperature T_X is in contact with a body Y at temperature T_Y different from T_X, the two bodies exchange energy in the form of heat. This exchange is all the more important as the difference in temperature, the contact surface and the contact time are large. A phenomenological law consists in writing that the heat received by X during $\mathrm{d}t$ is

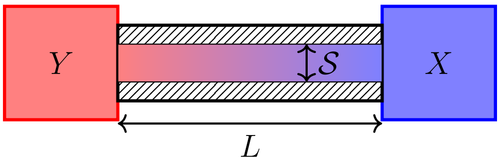
$$\delta Q = h\,\mathcal{S}\,(T_Y - T_X)\,\mathrm{d}t, \tag{2.4}$$

where $\mathcal{S}$ is the contact area h is the *heat transfer coefficient*. This coefficient depends on the materials constituting X and Y and on the quality of the contact.

Inside a material where the temperature is not homogeneous, we introduce the heat flux $\vec{q}$ (in W/m^2). The amount of heat that passes through an oriented surface $\overrightarrow{\mathrm{d}\mathcal{S}}$ during $\mathrm{d}t$ is then $\vec{q}\cdot\overrightarrow{\mathrm{d}\mathcal{S}}\,\mathrm{d}t$. Phenomenologically, for situations close to equilibrium, we write

$$\vec{q} = -\lambda\vec{\nabla}T, \qquad\qquad \text{(Fourier's law)}, \tag{2.5}$$

where λ (in W/m/K) is the thermal conductivity of the material.



The typical example where Fourier's law is used is the following: we consider two bodies X and Y at different temperatures, connected by a bar of length L and section $\mathcal{S}$. It is assumed that the bar is thermally isolated from the surroundings (but not from the two bodies X and Y). One can show that (2.5) implies that in the stationary regime (when nothing is time dependent), the temperature $T(x)$ in the bar at a distance x from the body Y varies linearly with x. By imposing $T(0) = T_Y$ and $T(L) = T_X$, we find

$$T(x) = T_Y - x\frac{T_Y - T_X}{L}.$$

The heat flux density is then given by $\vec{q} = (\lambda/L)(T_Y - T_X)\vec{e}_x$ and, therefore, the heat per unit of time (*i.e.* power) that crosses the bar is $(\lambda\mathcal{S}/L)(T_Y - T_X)$.

2.3.2 Heat exchange *via* a fluid (convection)

When substance is transported in a fluid, *i.e.* when there is macroscopic motion (a current), heat is transported with the fluid; it is convection. There are two types of convection:

Forced convection, when the fluid is set in motion externally. For example, blowing (*e.g.* to cool down soup) with a fan, *etc.*

Free convection, when the fluid motion starts spontaneously because the temperature is not uniform. For example, in a pot of water placed on fire, *convection cells* are created: hot water from the bottom of the pot rises to the surface, cools in contact with the atmosphere and goes down to warm up at the bottom of the pot.

Modelling convection phenomena is usually difficult. A simple case is that of a body X at temperature T_X in contact with a fluid Y (for example, the atmosphere) at a different temperature T_Y. Conduction and convection phenomena occur in a layer of fluid at the surface of the object. The thickness of this layer depends on the properties of the fluid. Then the heat exchanges can still be modelled by equation (2.4), where the coefficient h is now called the *conducto-convective coefficient*. This is Newton's law.

Video 4

2.3.3 Heat exchange by radiation

Electromagnetic radiation carries energy. When this radiation meets matter, it may, depending on its wavelength, be absorbed, be reflected or pass through. The substance that absorbs electromagnetic radiation obviously gains the corresponding energy.

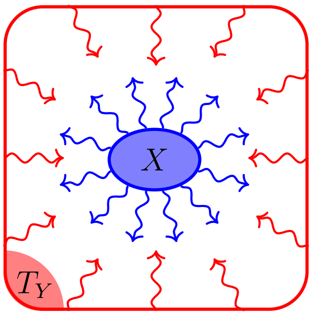
For each substance, a radiation absorption rate is defined as a function of its wavelength. A body that looks blue absorbs all wavelengths of the visible spectrum except those corresponding to blue. A body that looks black absorbs all the wavelengths of the visible spectrum.

The black body is defined as an ideal substance that perfectly absorbs radiation at all wavelengths (not just the visible ones!). It is demonstrated that each surface element $\mathrm{d}\mathcal{S}$ of a black body X of temperature T_X emits *spontaneously* an electromagnetic radiation of power

$$\mathrm{d}\mathcal{P} = \sigma T_X^4 \,\mathrm{d}\mathcal{S},$$

where $\sigma = 5.67\,10^{-8}\,\mathrm{W/m^2/K^4}$ is the Stefan-Boltzmann constant. It is the *black body radiation*. The wavelength distribution of the emitted radiation, and thus the perceived colour, depends on the temperature of the black body. It is this phenomenon which explains that the stars have different colours according to their temperatures. Black body radiation is in the infrared at ambient temperatures. It is a red glow just visible at 800 K; the sun emits as a black body at 5 000 K.

A real body emits as a black body only for the wavelengths it absorbs. (Hence a blue body does not emit spontaneously in the blue.) In practice, however, the black body remains a very good approximation for any substance.



If we have a body X (convex, to simplify) of surface $\mathcal{S}$ at temperature T_X in an environment at temperature T_Y (for example by putting it in an enclosure), two phenomena occur:

- The body X loses energy by black body radiation with a power $\sigma\mathcal{S}\,T_X^4$
- The body X absorbs the energy emitted by the environment. It is shown that the power received is simply $\sigma\mathcal{S}\,T_Y^4$.

By combining these two effects, the heat δQ gained by X during $\mathrm{d}t$ by radiation is written

$$\delta Q = \sigma\mathcal{S}(T_Y^4 - T_X^4)\,\mathrm{d}t.$$

Chapter 3

Video 1

Entropy and second law of thermodynamics

3.1 Necessity of the second law

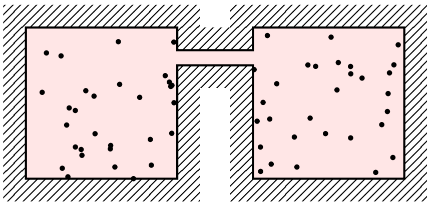
Video 2

The first law of thermodynamics (conservation of energy) sets limits on acceptable thermodynamic transformations: for an *isolated* system, a transformation from state (a) to state (b) is possible only if $U^{(a)} = U^{(b)}$ or, in other terms, if $\Delta U = 0$. According to the first law, if the transformation from (a) to (b) is possible, then the reverse from (b) to (a) is also possible.

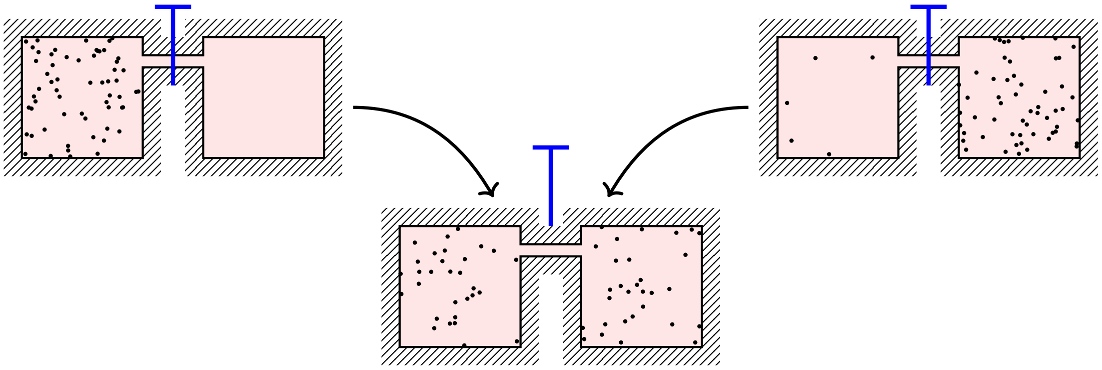
However, experience shows that for each system (and each choice of U, V, N, *etc.*) there exists only one well-defined equilibrium state, and that any isolated system evolves spontaneously and irreversibly towards this equilibrium state. *Hence, the first law of thermodynamics is not sufficient to explain this observation, and a second law is required to determine the equilibrium state.* Let us consider two examples of irreversible transformations.

3.1.1 Joule expansion

Let us consider a gas of n moles with an energy U in a chamber of volume V isolated from its surroundings. This chamber is separated into two equal parts of volume $V/2$ each and connected by a small pipe.



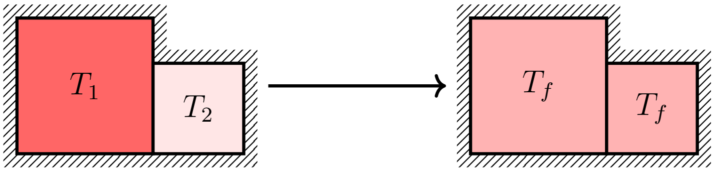
At equilibrium, each compartment contains $n/2$ moles and has an energy $U/2$. By installing a valve on the pipe, an operator can distribute as desired the n moles of the gas between the two compartments; for example, the operator may decide to put all (or almost all) the substance in one of the compartments and leave the other empty (or almost empty). However, as soon as the valve is opened (which can be done without heat or work), the system spontaneously relaxes to the equilibrium state; it is Joule's expansion.



The reverse transformation can not take place spontaneously.

3.1.2 Bodies in thermal contact

Let two bodies be initially separated and at equilibrium temperatures T_1 and T_2, with for example $T_1 > T_2$. They are brought together so they can exchange energy in the form of heat. It is always observed that heat goes from the hottest to the coldest body, until the temperatures equalize to an intermediate value T_f. The opposite is never observed whereas the first law does not exclude that the cold body can give heat to the hot body.



3.2 The second law

It is natural to characterize the equilibrium state as the state that maximizes "something". This "something" is entropy.

Video 3

Frame 3.1 : Entropy

For each system, there is a quantity S defined at equilibrium, called entropy, which is:

A state function

The value of S depends only on the (macroscopic) state of the system, not on its history. In simple cases, we write

$$S = S(U, V, n).$$

In more complicated cases (several compartments, several species, ...), entropy may depend on more variables.

Maximum at equilibrium

An isolated system (U, V, n are constant, there is no exchange of work nor heat with the surroundings) evolves towards an equilibrium state, compatible with the external constraints, for which S is maximum. In particular, when a constraint is lifted on an isolated system (two parts of the system are put into thermal contact, a valve is opened to let particles through, *etc.*), the system will tend towards a new equilibrium state and its entropy can only increase.

An additive quantity

For a system composed of two parts, we have

$$S_{\text{complete system}} = S_{\text{first part}} + S_{\text{second part}}.$$

Extensive

In most applications, entropy is an extensive quantity, see frame 1.4. However, this property is not essential and may be lost when one studies certain properties such as surface effects (surface tension) and gravitational effects (thermodynamics of a star or a galaxy).

Application: Let us recall example 3.1.2 (Bodies in thermal contact). The system is isolated and contains an internal energy U. U_1 is the internal energy of part (1), on the left; part (2), on the right, therefore has an energy $U_2 = U - U_1$ and the entropy of the system is written, by additivity,

$$S = S_1(U_1) + S_2(U - U_1), \tag{3.1}$$

where S_1 and S_2 are the entropies of part (1) and (2), respectively. (Of course, S_1 and S_2 also depend on other variables like N, V, …). Suppose that part (1) spontaneously gains energy $\mathrm{d}U_1$ in the form of heat from part (2). The new entropy is $S_1(U_1 + \mathrm{d}U_1) + S_2(U - U_1 - \mathrm{d}U_1)$ and an expansion allows one to obtain

$$\mathrm{d}S = \left[\frac{\partial S_1}{\partial U_1} - \frac{\partial S_2}{\partial U_2}\right] \mathrm{d}U_1. \tag{3.2}$$

The transformation is only possible if $\mathrm{d}S \geq 0$. We can deduce that

- If $\dfrac{\partial S_1}{\partial U_1} > \dfrac{\partial S_2}{\partial U_2}$, then $\mathrm{d}U_1 \geq 0$. Heat can only flow from (2) to (1).
- If $\dfrac{\partial S_1}{\partial U_1} < \dfrac{\partial S_2}{\partial U_2}$, then $\mathrm{d}U_1 \leq 0$. Heat can only flow from (1) to (2).

This example shows that $\partial S/\partial U$ must be a *decreasing* function $f(T)$ of the temperature (since the heat goes from the body having the smallest $\partial S/\partial U$ to the body having the largest $\partial S/\partial U$). For each choice of $f(T)$, a definition of the temperature is thus obtained. For this definition to coincide with the usual definitions of temperature, we must choose (and this is far from obvious!) $f(T) = 1/T$.

In the same way, by considering a system consisting of two parts separated by a piston, it can be shown that $\partial S/\partial V$ is connected to the pressure. Finally, when considering a porous partition, we find that $\partial S/\partial n$ is connected to the chemical potential. To make the link with what is already known from p and μ, we must have the following relations:

Video 4

Frame 3.2: First derivatives of entropy

For a system of n moles in a volume V with an energy U, the first derivatives of the function $S(U, V, n)$ are

$$\left.\frac{\partial S}{\partial U}\right|_{V,n} = \frac{1}{T}, \qquad \left.\frac{\partial S}{\partial V}\right|_{U,n} = \frac{p}{T}, \qquad \left.\frac{\partial S}{\partial n}\right|_{U,V} = -\frac{\mu}{T}, \tag{3.3}$$

where T, p and μ are respectively the temperature, the pressure and the chemical potential of the system. These three equations can be written in a more compact way using a differential:

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U + \frac{p}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}n. \tag{3.4}$$

This expression is called the **thermodynamic identity**.

A general consequence of this identity and the maximum principle is that:

- for two bodies in thermal contact, the energy (in the form of heat) goes from the warmest to the coldest,
- for two fluids at the same temperature separated by a piston, the volume goes from the fluid with lower pressure to the fluid with higher pressure,
- for two bodies at the same temperature separated by a porous partition, the particles migrate from the body with the greatest chemical potential to the body with the smallest chemical potential.

Remarks:

- We are considering the function $S(U, V, n)$. So, rather than writing $\partial S/\partial V\big|_{U,n}$, we could have written $\partial S/\partial V$ which means, unambiguously, "derivation with respect to V while keeping all the other variables constant."
- The differential (3.4) is a description of the properties of function S: if we consider two neighbouring states (U, V, n) and $(U + \mathrm{d}U, V + \mathrm{d}V, n + \mathrm{d}n)$, then we can calculate the difference in entropy $\mathrm{d}S$ between these two states. *The differential* (3.4) *describes the result of a transformation only when this one is quasistatic.*
- The quantities T, p and μ thus defined are also functions of U, V and n.
- These equalities imply that the unit for S is the joule per kelvin and that the unit for μ is the joule per mole.
- In statistical physics, the chemical potential is often written using a derivative of S with respect to N (number of particles) and not with respect to n (number of moles): $\mu = -T\,\partial S/\partial N$; in this case the unit of μ is the joule. The ratio between these two definitions of μ is the Avogadro constant.
- One needs to know how to adapt these properties to more complicated systems. For example, for a mixture of two species (1) and (2), the entropy depends on U, V, n_1 and n_2, and there are two chemical potentials μ_1 and μ_2.

Historically, the postulate did not appear as if by magic. Entropy was discovered in the 19th century as part of the study of thermal machines (motors, refrigerators). Major names associated with these discoveries include: Carnot, Clausius and Kelvin. The postulate was then expressed in the form of laws which all stated an impossibility, that is, in mathematical terms, an inequality. (This inequality is obviously equivalent to the statement of the postulate, even if it is not obvious.) We refer the reader to supplement A of the book on thermodynamics of Diu, Guthmann, Lederer and Roulet. The reading of Feynman's Lectures on Physics 2, Chapter 44 is also very interesting on this subject. The presentation in the form of a postulate, for example in the book of Callen, has the advantage of being very clear and concise.

3.3 Applications

3.3.1 Expression of $\mathrm{d}U$

The differential of U is obtained by inverting (3.4):

Frame 3.3 : **Differential of U**

For a system whose only variables are n, V and U, we have

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n. \tag{3.5}$$

In other words, the first derivatives of the function $U(S, V, n)$ are

$$\left.\frac{\partial U}{\partial S}\right|_{V,n} = T, \qquad \left.\frac{\partial U}{\partial V}\right|_{S,n} = -p, \qquad \left.\frac{\partial U}{\partial n}\right|_{S,V} = \mu. \tag{3.6}$$

For an ideal monoatomic gas, $U = \frac{3}{2}nRT$. However, we can not deduce from the previous frame that $\xcancel{p = 0}$ nor that $\xcancel{\mu = \frac{3}{2}RT}$. The reason is that (3.6) gives the derivatives of the function $U(S, V, n)$, at S constant, and not the derivatives of the function $U(T, V, n)$, at T constant.

Remarks:

- This expression must be adjusted when the system depends on different variables.
- During an infinitesimal transformation where n is fixed, generally $\mathrm{d}U = \delta Q + \delta W$. If the transformation is reversible, then $\mathrm{d}U$ is the internal energy difference between two neighbouring equilibrium points and $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$. Moreover, for a reversible transformation $\delta W = -p\,\mathrm{d}V$; therefore we deduce that

$$\delta Q_{\text{reversible}} = T\,\mathrm{d}S. \tag{3.7}$$

- In fact, we also have $\delta Q = T\,\mathrm{d}S$ for a quasistatic transformation at constant volume or such that $p = p_{\text{ext}}$. In particular, this is the case when the system under consideration is a heat bath (see frame 3.4 hereafter).

3.3.2 Positivity of C_V

Let us again consider the example of two bodies in thermal contact. When body (1) has an energy U_1 and body (2) an energy $U_2 = U - U_1$, the entropy is given by (3.1):

$$S = S_1(U_1) + S_2(U - U_1).$$

The system is considered at equilibrium, that is to say that

$$\frac{1}{T_1} = \frac{\partial S_1}{\partial U_1} = \frac{\partial S_2}{\partial U_2} = \frac{1}{T_2}.$$

We assume as before that part (1) gains energy $\mathrm{d}U_1$ from part (2) and we would like to calculate $\mathrm{d}S$. The expression (3.2) of $\mathrm{d}S$ is not sufficient since the term in $\mathrm{d}U_1$ is null, and it is necessary to develop to the second order:

$$\mathrm{d}^2 S = \frac{1}{2}\left[\frac{\partial^2 S_1}{\partial U_1^2} + \frac{\partial^2 S_2}{\partial U_2^2}\right](\mathrm{d}U_1)^2.$$

This quantity is necessarily negative: the system has been assumed to be in equilibrium, entropy is at a maximum, and any change in the state of the system (a non-zero $\mathrm{d}U_1$) must lead to a decrease in entropy.

A reasoning on extensivity shows that, in the limit of the size of body (2) tending to infinity, we have $\partial^2 S_2/\partial U_2^2 \to 0$ (see also the calculation hereafter). We can then deduce that for body (1), whatever it is, we must have

$$\frac{\partial^2 S}{\partial U^2} \leq 0,$$

where we have written S and U rather than S_1 and U_1, for simplicity. The function S is necessarily concave in U. In fact, we can generalize this argument and show that

S is a concave function of all its variables.

So, for any system, we have

$$\frac{\partial^2 S}{\partial U^2} = \frac{\partial}{\partial U}\left[\frac{1}{T}\right] = -\frac{1}{T^2}\frac{\partial T}{\partial U} = -\frac{1}{C_V T^2},$$

where $C_V = \partial U/\partial T$ (here a constant V and n are implied) is the heat capacity at constant volume. It is an extensive quantity. (In particular, if the size of the system tends to infinity, then $C_V \to \infty$ and $\partial^2 S/\partial U^2 \to 0$, as predicted). We have just demonstrated that

$$C_V \geq 0.$$

We will see several other relations of the same type in chapter 4.

3.3.3 Entropy of an ideal gas

For an ideal monoatomic gas (for example helium or argon) the equation of state and the value of the internal energy are known, see frame 1.5:

$$pV = nRT, \qquad U = \frac{3}{2}nRT.$$

From these two expressions, $1/T$ and p/T can be extracted and injected into the thermodynamic identity:

$$\mathrm{d}S = \frac{3}{2}nR\frac{\mathrm{d}U}{U} + nR\frac{\mathrm{d}V}{V} - \frac{\mu}{T}\mathrm{d}n.$$

Only the expression of μ seems to be missing. To get by, we start by assuming that n is a fixed parameter, and that the only real variables of S are U and V. The differential can then be written

$$\mathrm{d}S = \frac{3}{2}nR\frac{\mathrm{d}U}{U} + nR\frac{\mathrm{d}V}{V} = \mathrm{d}\Big[\frac{3}{2}nR\ln U + nR\ln V\Big],$$

and so, after integration,

$$S = \frac{3}{2}nR\ln U + nR\ln V + \text{“constant”}.$$

Here, the integration constant is a constant with respect to the variables U and V over which we have just integrated, but it can also depend on the parameter n. Hence, we will write it in the form $f(n)$, where f is an unknown function to determine:

$$S(U,V,n) = \frac{3}{2}nR\ln U + nR\ln V + f(n). \tag{3.8}$$

It is important to understand that this unknown function $f(n)$ depends only on the amount of substance n and certainly not on U or V. To further determine the entropy, we will use the property of extensivity: if system (A) is of the same nature as system (B) but is λ times larger, *i.e.* if (A) has λ times more substance than (B), occupies λ times more volume and has λ times more energy, then the entropy of (A) is λ times larger. This can be written as an equation:

$$S(\lambda U, \lambda V, \lambda n) = \lambda S(U,V,n).$$

But, according to (3.8),

$$\begin{aligned}
S(\lambda U, \lambda V, \lambda n) &= \frac{3}{2}\lambda nR\ln(\lambda U) + \lambda nR\ln(\lambda V) + f(\lambda n),\\
&= \frac{3}{2}\lambda nR\big(\ln\lambda + \ln U\big) + \lambda nR\big(\ln\lambda + \ln V\big) + f(\lambda n),\\
&= \lambda\Big[\frac{3}{2}nR\ln U + nR\ln V\Big] + \frac{5}{2}\lambda nR\ln\lambda + f(\lambda n).
\end{aligned}$$

Comparing with the expression of $\lambda S(U,V,n)$, we find that the function f must verify

$$\frac{5}{2}\lambda nR\ln\lambda + f(\lambda n) = \lambda f(n).$$

We can find the solution to this equation by choosing $\lambda = 1/n$. We then obtain

$$f(n) = n\Big[f(1) - \frac{5}{2}R\ln n\Big].$$

$f(1)$ is a constant, independent of U, V or n. It can however depend on the type of monoatomic gas used. We write $f(1) = Rc$ to enable factorization by R and we obtain, in (3.8),

$$S(U,V,n) = nR\left[\frac{3}{2}\ln U + \ln V - \frac{5}{2}\ln n + c\right] = nR\left[\frac{3}{2}\ln\frac{U}{n} + \ln\frac{V}{n} + c\right]. \tag{3.9}$$

(The right-hand side of the equation shows immediately that S is extensive.)

! In general, the argument of a mathematical function (exp, sin, tan, ...) must be a dimensionless number: hence the expression $\xcancel{\exp(1\,\mathrm{kg})}$ has no meaning. For this reason, some consider that we should not write $\ln U$, but rather $\ln \frac{U}{u_0}$ where u_0 is a constant energy (for example: $u_0 = 1\,\mathrm{J}$). But, formally, the properties of the logarithm allow us to write $\ln \frac{U}{u_0} = \ln U - \ln u_0$ and, in a sense, to integrate $\ln u_0$ into the unknown constant c. We therefore allow ourselves to write $\ln U$, knowing that c contains a term correcting this expression. As a result, the constant c cannot be dimensionally analysed, and its value depends on the unit of energy chosen to calculate $\ln U$.

3.3.4 Reservoirs: thermostat, pressostat

Frame 3.4 : **Reservoirs**

- A *heat bath*, or *thermostat* is a system that can receive or provide heat without changing its own temperature:

$$\mathrm{d}T_{\mathcal{R}} = 0 \qquad \text{whatever } \delta Q_{\mathcal{R}}$$

$T_{\mathcal{R}}$: temperature of the heat bath
$\delta Q_{\mathcal{R}}$: heat received by the bath

- A *volume reservoir*, or *pressostat* is a system whose volume may change without its pressure changing.

$$\mathrm{d}p_{\mathcal{R}} = 0 \qquad \text{whatever } \mathrm{d}V_{\mathcal{R}}$$

$p_{\mathcal{R}}$: reservoir pressure
$\mathrm{d}V_{\mathcal{R}}$: volume received by the reservoir

- A *particle reservoir* or *substance reservoir* is a system that can receive or supply heat and substance without changing its temperature or chemical potential.

$$\mathrm{d}T_{\mathcal{R}} = 0,\ \mathrm{d}\mu_{\mathcal{R}} = 0 \qquad \text{whatever } \delta Q_{\mathcal{R}} \text{ and } \mathrm{d}n_{\mathcal{R}}$$

$\mu_{\mathcal{R}}$: reservoir chemical potential
$\mathrm{d}n_{\mathcal{R}}$: amount of substance received by the reservoir

A reservoir is always assumed to be in internal equilibrium (all thermodynamic variables are therefore well defined). The transformations undergone by a reservoir are therefore always assumed quasistatic.

Remarks:

- Reservoirs are ideal systems, and only approximations can be made.
- In general, a physical reservoir is a "big" system. For example, the ocean is an excellent thermostat (if an exothermic reaction in a test tube occurs in the ocean, the ocean will receive heat from the reaction but its temperature will not change). Similarly, the atmosphere makes an excellent pressostat.
- An example of a "small" thermostat is a mixture of water and ice, which is necessarily at 0° C: if heat is supplied to this system, some ice will melt, but the temperature will not change. Similarly, when cooking, a "bain marie" is a thermostat at 100° C.

Imagine a system of study (whose variables are denoted S, U, V, p, T, *etc.*) which exchanges energy and volume with a heat bath $\mathcal{R}$ (of variables $S_{\mathcal{R}}$, $U_{\mathcal{R}}$, $T_{\mathcal{R}}$, *etc.*). One can choose to consider the whole set (*i.e.* $\{\text{system} + \text{reservoir}\}$) as isolated.

For a heat bath, you can always write

$$\mathrm{d}S_{\mathcal{R}} = \frac{\delta Q_{\mathcal{R}}}{T_{\mathcal{R}}},$$

with $\delta Q_{\mathcal{R}}$ the heat received by the reservoir. As the set $\{\text{system} + \text{reservoir}\}$ is isolated, we have

$$\delta Q + \delta Q_{\mathcal{R}} = 0,$$

with δQ the heat received by the system. We can deduce that

$$\mathrm{d}S_{\mathcal{R}} = -\frac{\delta Q}{T_{\mathcal{R}}} \qquad \text{and} \qquad \Delta S_{\mathcal{R}} = -\frac{Q}{T_{\mathcal{R}}}$$

(We used the fact that $T_{\mathcal{R}}$ is constant to integrate. One needs to pay attention to the fact that Q is the heat received by the system, the heat received by the reservoir being $-Q$.)

By using $\Delta S + \Delta S_{\mathcal{R}} \geq 0$ (the entropy of the universe can only increase), we finally obtain:

Frame 3.5 : **Minimal increase of entropy**

For any system in contact with a single heat bath at temperature $T_{\mathcal{R}}$ and which receives, during a transformation, heat Q from this reservoir, we have

$$\Delta S \geq \frac{Q}{T_{\mathcal{R}}},$$

the equality being valid only for a reversible transformation.

Remarks:

- This inequality and its generalizations are called “Clausius inequalities”.
- This inequality remains valid if the heat bath is also a volume and / or substance reservoir.
- If the system undergoes a quasistatic transformation at constant temperature T, then $\Delta S = Q/T \geq Q/T_{\mathcal{R}}$. Which means $Q \geq 0$ if $T \leq T_{\mathcal{R}}$ and $Q \leq 0$ if $T \geq T_{\mathcal{R}}$.
- If the system is in contact with three baths of temperature T_1, T_2 and T_3, and it receives heat Q_1, Q_2 and Q_3 from these three reservoirs, the above is generalized to

$$\Delta S \geq \frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3}.$$

In general, if there is an infinity of reservoirs, we can write

$$\Delta S \geq \int \frac{\delta Q}{T_{\text{ext}}}.$$

3.4 Microscopic interpretation

Video 5

The microscopic interpretation of the internal energy is carried out microscopic configuration by microscopic configuration: if the microscopic configuration of a system is known, that is to say if all the positions and momenta of the particles are known, then it is possible to calculate the (mechanical) energy that results as a sum of the kinetic energy and the interaction potential. We can talk about the energy of *a single* configuration.

Entropy has no equivalent interpretation: it is not a mechanical quantity, and we cannot speak of the entropy of *a* microscopic configuration. Entropy is a quantity related to *all* the microscopic configurations accessible to the system, and their probabilities: it is a statistical quantity.

The basic idea is that for a gas, at U, V and n fixed, there are a lot of accessible microscopic configurations, that is, ways of deciding where the particles are and what their velocities are, knowing that we count only the configurations having the correct energy and the correct number of particles in the correct volume. If we look at the system at a given moment, we will see a configuration. If we leave for a coffee and come back to observe the same system, we will see another configuration, completely different. Of course, the laws of classical mechanics allow, in theory, to calculate what should be the second configuration from the first, but this calculation is not feasible and, in practice, for each observation, we have a configuration that seems to be drawn at random. The important question is therefore, what is the probability of each configuration?

The statistical interpretation of entropy is done in two postulates.

Frame 3.6 : Statistical interpretation of entropy

We consider an *isolated* system (so U, V and n are fixed, in simple cases) and we write

$$\varOmega = \left[\begin{array}{l}\text{The number of microscopic configurations}\\ \text{accessible to the system given } U,\, V,\, n,\, \dots\end{array}\right].$$

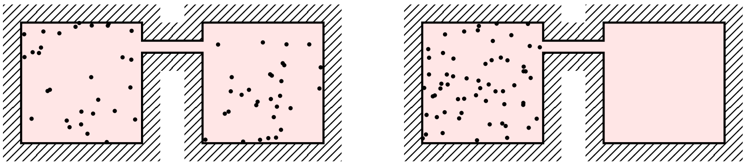
Then, at thermodynamic equilibrium,

- All accessible microscopic configurations are equiprobable.
- The entropy of the system is
$$S = k_B \ln \varOmega.$$

Remarks:

- If we change U, V or n, the number of accessible microscopic configurations changes. $\varOmega$ and S are therefore functions of U, V, n, …
- Since the $\varOmega$ states are assumed equiprobable, the probability of each one of them is, by normalization, $1/\varOmega$.
- In classical mechanics, mathematically there is an infinity of microscopic configurations: each coordinate is a real number, and there is an infinity of real numbers in each interval. To obtain a finite $\varOmega$, one must make the physical assumption that the positions and momenta are known with a finite number of digits after the decimal point. In quantum mechanics, $\varOmega$ counts the (finite) number of eigenstates of the Hamiltonian with an energy (roughly) equal to U.

These axioms are often rather disturbing at first sight: what we are saying is that in the system of example 3.1.1, the following two microscopic configurations are equiprobable at equilibrium:



However, we know that it is essentially impossible for all the particles to be on the left side. It is important to understand why:

> Each individual configuration has the same probability, but there are ***many more*** configurations where the particles are well distributed in both sides rather than configurations where they are all on the left.

Let us do the math using the following notation:

- Ω the total number of microscopic configurations,
- Ω_{left} the number of configurations where all the particles are on the left,
- $N = n\mathcal{N}_A$ the number of particles present in the system.

The probability of having all the particles on the left is on the one hand $1/2^N$ (because each one of the N particles has a one in two chance of being on the left) and on the other hand $\Omega_{\text{left}}/\Omega$ (number of favourable configurations divided by total number of configurations). So we have

$$\Omega = 2^N \Omega_{\text{left}}.$$

This factor 2^N, with N of the order of 10^{20}, is an unreasonably large number. The probability $1/2^N$ that all the particles are on the left is essentially equal to zero, because the corresponding configurations are extremely rare.

Suppose we put a valve on the pipe and prepare the system with all the particles on the left. The number of accessible configurations is Ω_{left} and the entropy of the system is

$$S_{\text{all particles on the left}} = k_B \ln \Omega_{\text{left}}.$$

We then open the valve and wait for equilibrium. The number of accessible configurations is now Ω, which is much larger, and the new entropy is

$$S_{\text{particles are everywhere}} = k_B \ln \Omega.$$

Then by choosing a configuration at random, we are quite certain to choose one where the particles are well distributed because these configurations are very much in the majority. The fact of having opened the valve led to an irreversible evolution of the system towards a new equilibrium state where the particles are well distributed. This irreversible evolution is accompanied by an increase in entropy given by

$$\Delta S = k_B \ln \Omega - k_B \ln \Omega_{\text{left}} = k_B \ln 2^N = N k_B \ln 2 = nR \ln 2.$$

It is easy to verify that this is the result obtained by doing $\Delta S = S(U, 2V, n) - S(U, V, n)$ from expression (3.9) of the entropy of an ideal gas.

Video 1

Chapter 4

Thermodynamic functions and potentials

In this chapter, we present the first applications of the two laws: the thermodynamic potentials, the state functions resulting from the Legendre transformations and the definition of the calorimetric coefficients.

4.1 Thermodynamic potentials

4.1.1 Definition

The evolution criterion towards equilibrium of an *isolated* system is known: according to the second law, the entropy S of *the system* becomes maximal. For a *non-isolated* system, one must use the entropy of *the universe* S_{univ}, the value of which is inconvenient to work with.

In this section, we therefore consider a system that is *a priori* not isolated and which is at least in contact with a heat bath of (constant) temperature T_0. The *thermodynamic potential* is then a function $\varPhi$ such that, for any transformation,

$$\Delta\varPhi = -T_0 \Delta S_{\text{univ}}. \tag{4.1}$$

By direct interpretation of the second law, the thermodynamic potential is a function which decreases during an irreversible natural transformation to reach its minimum at thermodynamic equilibrium and that remains constant during a reversible transformation.

For a given system, there are as many thermodynamic potentials as there are possible external situations: with or without pressostats, with or without generators, with or without reservoirs, *etc.* A difficulty is therefore, for a given situation, to find the "good potential". Strictly speaking, the thermodynamic potential is not a state function of the system, but remains a state function of the universe. The two most common cases are:

Frame 4.1 : **Thermodynamic potentials**

- For a system only in contact with a heat bath of temperature T_0,

$$\varPhi = U - T_0 S. \tag{4.2}$$

- For a system only in contact with a heat bath of temperature T_0 and a volume reservoir of pressure p_0

$$\varPhi = U - T_0 S + p_0 V. \tag{4.3}$$

For any transformation, then $\Delta\Phi = -T_0\Delta S_{\text{univ}}$. The thermodynamic equilibrium is thus reached when Φ is minimal.

Indeed, the heat received by the heat bath is $T_0\Delta S_{\text{therm}}$, so the heat received by the system is $Q = -T_0\Delta S_{\text{therm}}$.

- In the case of a system in contact with only one heat bath, we have $W = 0$ (there is no work) and therefore $\Delta U = Q = -T_0\Delta S_{\text{therm}}$. As expected, we then obtain $\Delta\Phi = \Delta U - T_0\Delta S = -T_0(\Delta S + \Delta S_{\text{therm}}) = -T_0\Delta S_{\text{univ}}$.
- In the case of a system in contact with a heat bath and a volume reservoir, the system receives work: $W = -p_0\Delta V$; we therefore have $\Delta U = -T_0\Delta S_{\text{therm}} - p_0\Delta V$. From this we deduce $\Delta\Phi = \Delta U - T_0\Delta S + p_0\Delta V = -T_0(\Delta S + \Delta S_{\text{therm}}) = -T_0\Delta S_{\text{univ}}$ as expected.

Remark: The potential Φ depends on T_0, p_0 (in the case of a volume reservoir) and on the state of the system that can be characterized by the variables of our choice, for example $(U, n, V, \ldots)$, or $(S, n, V, \ldots)$ or $(T, n, V, \ldots)$.

4.1.2 Using the potential to determine equilibrium

Situation where there is contact with only one heat bath

We consider a system made of rigid and impervious walls (n and V are fixed) in contact with a heat bath. The suitable potential is $\Phi = U - T_0S$. The system is assumed to be already in internal equilibrium and we are looking for the equilibrium conditions with the surroundings. At thermodynamic equilibrium, Φ is minimal and therefore its differential is zero:

$$\mathrm{d}\Phi = \mathrm{d}U - T_0\,\mathrm{d}S = 0.$$

To go further, we must choose which variable to use to characterize the system.

- If we choose U, then we write $\mathrm{d}S = \frac{1}{T}\,\mathrm{d}U$ and

$$\mathrm{d}\Phi = \left(1 - \frac{T_0}{T}\right)\mathrm{d}U = 0.$$

- If we choose S, then we write $\mathrm{d}U = T\,\mathrm{d}S$ and

$$\mathrm{d}\Phi = (T - T_0)\,\mathrm{d}S = 0.$$

- If we choose T, then we write $\mathrm{d}U = C_V\,\mathrm{d}T$ and $\mathrm{d}S = C_V\,\frac{\mathrm{d}T}{T}$ (we will come back to these equations later in frame 4.4) and we get

$$\mathrm{d}\Phi = \left(1 - \frac{T_0}{T}\right)C_V\,\mathrm{d}T = 0.$$

We reach the same conclusion, whatever the choice of variable (fortunately!): In thermodynamic equilibrium, we have

$$T = T_0.$$

Situation where there is contact with a heat bath and a volume reservoir

A homogeneous fluid is considered in contact with a heat bath and a volume reservoir. The adapted thermodynamic potential is $\Phi = U - T_0 S + p_0 V$. The fluid is assumed to be already in internal equilibrium and we are looking for the equilibrium conditions with the surroundings. At thermodynamic equilibrium, Φ is minimal and therefore its differential is zero:

$$\mathrm{d}\Phi = \mathrm{d}U - T_0\,\mathrm{d}S + p_0\,\mathrm{d}V = 0. \tag{4.4}$$

To go further, we must choose which variables to use to characterize the system. If we choose U and V (and other variables like n), we use the thermodynamic identity $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V$ and we obtain

$$\mathrm{d}\Phi = (T - T_0)\mathrm{d}S - (p - p_0)\mathrm{d}V = 0. \tag{4.5}$$

The equilibrium condition between the system and the heat bath is, of course,

$$T = T_0, \qquad p = p_0.$$

As in the first case, other choices of variables are possible. For example, if we choose T and V and, anticipating a little the end of the chapter, we use in (4.4) the definitions of the calorimetric coefficients (4.21) and (4.22), we arrive at

$$\mathrm{d}\Phi = \left(1 - \frac{T_0}{T}\right) C_V\,\mathrm{d}T + \left[\left(1 - \frac{T_0}{T}\right)\ell - p + p_0\right]\mathrm{d}V = 0. \tag{4.6}$$

The cancellation of the terms in factor of $\mathrm{d}T$ and $\mathrm{d}V$ restores the conditions $T = T_0$ and $p = p_0$. The thermodynamic potential is therefore minimal with respect to any set of variables.

4.1.3 First introduction of thermodynamic functions

We consider a fluid (for simplicity) characterized by the variables $\{U, V, n\}$. For each value of $\{U, V, n\}$, we can calculate the temperature $T(U, V, n)$ of the system, the entropy $S(U, V, n)$ of the system, *etc.*

A quantity of this fluid is placed in an impervious and rigid recipient in contact with only one thermostat at temperature T_0. The values of V and n are fixed, the energy U is not (the system exchanges heat with the thermostat) and we want to determine the equilibrium value U_{eq} of the energy.

As we have just seen, the equilibrium is described by the state which minimizes the potential $\Phi = U - T_0 S$, and the above calculation shows that it is obtained by writing $T = T_0$. More precisely, we write that U_{eq} is such that $T(U_{\text{eq}}, V, n) = T_0$, which allows to obtain U_{eq} as a function of V, n and T_0.

The minimum *value* of Φ (therefore, reached at equilibrium) is called *the free energy* F of the system:

$$F = U_{\text{eq}} - T_0 S_{\text{eq}} = U_{\text{eq}} - T_0 S(U_{\text{eq}}, V, n).$$

It is important not to confuse Φ and F:

- the potential Φ is a function of *four variables:* a variable T_0 which describes the heat bath, and three variables $\{U, V, n\}$ which describe the system. It is defined whether or not the system is at equilibrium with the heat bath.

- The free energy F is a function of *three variables:* T_0, V and n. Indeed, the value U_{eq} of the energy at equilibrium is itself a function of T_0, V and n. The free energy characterizes a system at equilibrium with a heat bath.

By definition, F is the minimum value of $\varPhi$ over all possible choices of U; hence we have

$$F(T_0, V, n) = \min_U \varPhi(T_0, U, V, n) = \min_U \big[U - T_0 S(U, V, n)\big]. \tag{4.7}$$

Or, we can simply write

$$F(T, V, n) = U_{\text{eq}} - T S_{\text{eq}}, \tag{4.8}$$

where U_{eq} and S_{eq} are the equilibrium values of the energy and entropy of the system when it is at temperature T (assuming V and n are fixed). One way to set the temperature of the system is to put it in contact with a heat bath (and then we have $T = T_0$), but we can always define F using (4.8), even if there is no heat bath.

From a mathematical point of view, the function F obtained from (4.7) or (equivalently) from (4.8) is the Legendre transformation of the function $U(S, V, n)$ with respect to the variable S. This is a mathematical operation which plays an important role in thermodynamics and that we will study in detail in the following section.

In the same way, if the system is in contact with a heat bath (at temperature T_0) and a volume reservoir (at pressure p_0), the values of U and V are determined by the equilibrium condition that the (suitable) potential $\varPhi = U - T_0 S + p_0 V$ is minimal. This potential depends on the five variables $\{T_0, p_0\}$ and $\{U, V, n\}$. The *value* of the minimum potential is called the *free enthalpy or Gibbs free energy* G, which is a function of the three variables $\{T_0, p_0\}$ and n. We can write:

$$G(T_0, p_0, n) = \min_{U,V} \big[U - T_0 S(U, V, n) + p_0 V\big] \tag{4.9}$$

or, equally,

$$G(T, p, n) = U_{\text{eq}} - T S_{\text{eq}} + p V_{\text{eq}}, \tag{4.10}$$

where U_{eq}, S_{eq} and V_{eq} are the equilibrium values of the system when it is at temperature T and at pressure p.

4.1.4 Internal variables

Consider again a system in contact with a heat bath. This system is described by the variables $\{U, V, n\}$ and by an additional internal variable X. (For example, X can be the position of a piston or the fraction of energy in the left part of a system, *etc.*)

To find the equilibrium, the thermodynamic potential $\varPhi = U - T_0 S$ must be minimized with respect to U and X:

$$\left.\frac{\partial \varPhi}{\partial U}\right|_{V,n,X} = 0 \qquad \left.\frac{\partial \varPhi}{\partial X}\right|_{V,n,U} = 0.$$

As before, the first condition leads to an internal equilibrium energy U_{eq} such that $T = T_0$. By introducing this value of U_{eq} in $\varPhi$, we obtain the free energy F and the second condition becomes:

$$\left.\frac{\partial F}{\partial X}\right|_{V,n,T} = 0.$$

We thus obtain the following result and its generalization:

Frame 4.2 : Thermodynamic equilibrium in terms of F and G

- The equilibrium of a system in contact with a heat bath only is such that the temperature is equal to the temperature of the heat bath and the internal variables minimize the free energy F.
- The equilibrium of a system in contact with a heat bath and a volume reservoir is such that the temperature of the system is equal to the temperature of the heat bath, the pressure is equal to the one of the volume reservoir, and the internal variables minimize the Gibbs free energy G.

4.2 Legendre transformation

The thermodynamic identity written in the form of $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \cdots$ poses a technical problem: the entropy S is not an easy variable to control. Its conjugate variable, the temperature $T = \partial U/\partial S$, is clearly preferable. The Legendre transformation makes it possible to substitute these variables without loss of information.

4.2.1 Mathematical presentation

Let x be a variable and $f(x)$ a function. Then let y be the variable such that $y = f'(x) = y(x)$. We want to replace the information content of function $f(x)$ by the content of a function of y. One could imagine doing a direct substitution:

$$y = y(x) \quad \Longrightarrow \quad x = x(y) \quad \text{and we write} \quad g(y) = f[x(y)].$$

But the flaw of this operation is that there is a "loss of information". Let us try to do the reverse operation: let $g(y)$ be known, we are looking for the function $f(x)$ such that

$$y(x) = f'(x) \quad \text{and} \quad f(x) = g[y(x)] \quad \Longrightarrow \quad f(x) = g[f'(x)].$$

Besides the fact that the differential equation $f(x) = g\big[f'(x)\big]$ is not necessarily easy to solve, there is an insoluble problem of constant determination: there are several solutions. We prefer to use the Legendre transformation by introducing a new function

$$h(y) = \min_x \big[f(x) - xy\big]. \tag{4.11}$$

In practice, to calculate $h(y)$, we must find the value $x(y)$ which minimizes $f(x) - xy$, the value of y being fixed. Because it is a minimum, the derivative of $f(x) - xy$ with respect to x must be zero when $x = x(y)$ and so we obtain

$$h(y) = f\big[x(y)\big] - x(y)y \qquad \text{where } x(y) \text{ is defined by} \quad f'\big[x(y)\big] - y = 0. \tag{4.12}$$

In practice, to be able to carry out calculations efficiently, one gains to be a little slack on the notation: the variables y and x are conjugated through the equality $y = f'(x)$. In some cases, we can think of y as a function of x, and in other cases we will think of x as a function of y (that is, we simply write as x what was written above as $x(y)$). Then we can simply write

$$\begin{aligned} h(y) &= f - xy \qquad \text{with } y = f'(x) \\ &= f(x) - xf'(x) = -x^2 \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{f(x)}{x}\right), \end{aligned} \tag{4.13}$$

where x is to be understood as a function of y. To calculate $h'(y)$, the simplest method is to consider the differential; using $\mathrm{d}f = y\,\mathrm{d}x$, we get

$$\mathrm{d}h = \mathrm{d}(f - xy) = \mathrm{d}f - x\,\mathrm{d}y - y\,\mathrm{d}x = -x\,\mathrm{d}y, \tag{4.14}$$

and therefore $x = -h'(y)$. Exercise: obtain this result from (4.12).

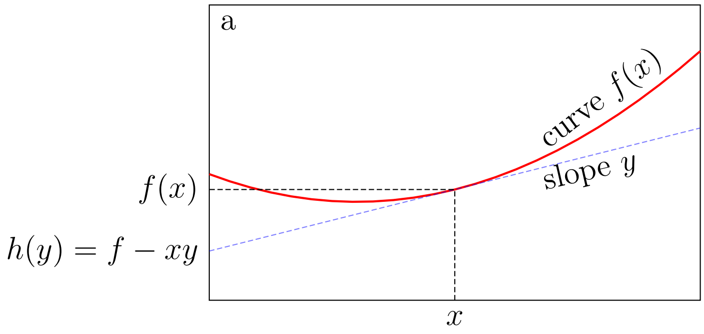
It is easy to reverse the Legendre transformation: given $h(y)$, how do we recover $f(x)$? We simply write

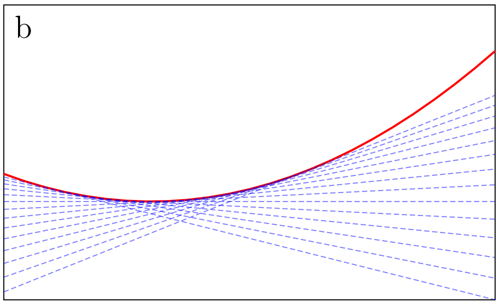
$$\begin{aligned} f(x) &= h + xy \qquad \text{with } x = -h'(y) \\ &= h(y) - yh'(y) = -\,y^2 \frac{\mathrm{d}}{\mathrm{d}y}\left(\frac{h(y)}{y}\right), \end{aligned} \tag{4.15}$$

where y is to be understood as a function of x.

Note the simplicity: the reverse transformation of the Legendre transformation is (to within a sign factor) the Legendre transformation itself. In fact, it can easily be verified that $f(x) = \max_y \big[h(y) + xy\big]$, to compare with (4.11).

The Legendre transformation has a geometric interpretation. Knowing the function $f(x)$, its graphical representation can be drawn; $y = f'(x)$ is the slope of the tangent of the curve at x and $h(y) = f - xy$ is the intersection of this tangent with the y axis (figure a). Conversely, knowing the function $h(y)$, for each value of y, the line of slope y and y-intercept $h(y)$ can be plotted. The curve of $f(x)$ can be reconstructed as the envelope of all these lines (figure b).





4.2.2 Application to thermodynamics

Frame 4.3 : The thermodynamic functions

Video 2

Let there be a system where the internal energy is written $U = U(S, V, X_1, X_2, \dots)$, such that

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + Y_1\,\mathrm{d}X_1 + Y_2\,\mathrm{d}X_2 + \cdots$$

By Legendre transformations, the following state functions are defined:

- Free energy $F(T, V, X_1, X_2, \dots) = U - TS.$
- Enthalpy $H(S, p, X_1, X_2, \dots) = U + pV.$
- Gibbs free energy $G(T, p, X_1, X_2, \dots) = U - TS + pV.$

The differentials of these functions are deduced from the differential of U:

$$\begin{aligned}
\mathrm{d}F &= -S\,\mathrm{d}T - p\,\mathrm{d}V + Y_1\,\mathrm{d}X_1 + Y_2\,\mathrm{d}X_2 + \cdots \\
\mathrm{d}H &= \quad T\,\mathrm{d}S + V\,\mathrm{d}p + Y_1\,\mathrm{d}X_1 + Y_2\,\mathrm{d}X_2 + \cdots \\
\mathrm{d}G &= -S\,\mathrm{d}T + V\,\mathrm{d}p + Y_1\,\mathrm{d}X_1 + Y_2\,\mathrm{d}X_2 + \cdots
\end{aligned} \tag{4.16}$$

Remarks:

- A large number of relations can be deduced from the differentials (4.16). Here are some first derivatives:

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,\{X_n\}} = -\left.\frac{\partial G}{\partial T}\right|_{p,\{X_n\}} \qquad V = \left.\frac{\partial H}{\partial p}\right|_{S,\{X_n\}} = \left.\frac{\partial G}{\partial p}\right|_{T,\{X_n\}}$$

$$Y_n = \left.\frac{\partial F}{\partial X_n}\right|_{T,V,\{X_{m\neq n}\}} = \left.\frac{\partial H}{\partial X_n}\right|_{p,S,\{X_{m\neq n}\}} = \left.\frac{\partial G}{\partial X_n}\right|_{p,T,\{X_{m\neq n}\}}$$

  and some Maxwell equations (one for F, one for G and one for H)

$$\left.\frac{\partial p}{\partial T}\right|_{V,\{X_n\}} = \left.\frac{\partial S}{\partial V}\right|_{T,\{X_n\}} \qquad -\left.\frac{\partial S}{\partial X_n}\right|_{T,\{X_{m\neq n}\}} = \left.\frac{\partial Y_n}{\partial T}\right|_{\{X_n\}} \qquad -\left.\frac{\partial S}{\partial p}\right|_{T,\{X_n\}} = \left.\frac{\partial V}{\partial T}\right|_{p,\{X_n\}}$$

- The free energy F of a system that does not depend on the volume V can of course be defined.
- The free energy F is the Legendre transformation of U for the pair of variables $(S, T = \partial U/\partial S)$. The enthalpy H is the Legendre transformation of U for the pair of variables $(V, -p = \partial U/\partial V)$. The Gibbs free energy G can be seen either as the Legendre transformation of F for the pair of variables $(V, -p = \partial F/\partial V)$, or as the Legendre transformation of H for the pair of variables $(S, T = \partial H/\partial S)$.

$$\begin{tikzcd}
& F \arrow[dr, leftrightarrow, "V", "p"'] & \\
U \arrow[ur, leftrightarrow, "S", "T"'] \arrow[dr, leftrightarrow, "V", "p"'] & & G \\
& H \arrow[ur, leftrightarrow, "S", "T"'] &
\end{tikzcd}$$

- The relation (4.15) applied to F and G constitutes the Gibbs-Helmholtz equations:

$$U = -T^2 \frac{\partial (F/T)}{\partial T}\bigg|_{V,\{X_n\}} \qquad\qquad H = -T^2 \frac{\partial (G/T)}{\partial T}\bigg|_{p,\{X_n\}} \tag{4.17}$$

- Let a system exchange heat with a thermostat at temperature T_0, and receive work W. According to the first law, $\Delta U = Q + W$, with $Q = -T_0\,\Delta S_{\text{therm}}$. It is assumed that, in the initial and final states, the system is in equilibrium with the thermostat, and therefore has a temperature $T = T_0$. Then,

$$\Delta F = \Delta U - \Delta(TS) = Q + W - T_0\Delta S = W - T_0(\Delta S_{\text{therm}} + \Delta S) = W - T_0\Delta S_{\text{univ}} < W,$$

according to the second law. It is assumed that the operator wants to recover work (and therefore that $W < 0$). This inequality puts a limit on the work that is recoverable: $|W| < -\Delta F$. Therefore, during a monothermal transformation, the energy of a system "that can be released" is the variation of the free energy, hence its name.
- The enthalpy can be interpreted as follows: Let a system exchange heat and evolve in contact with an external pressostat of pressure p_0. According to the first law, $\Delta U = Q + W$, with $W = -\,p_0\Delta V$. It is assumed that in the initial and final states, the system is in equilibrium with the pressostat, therefore with pressure $p = p_0$. Then,

$$\Delta H = \Delta U + \Delta(pV) = Q + W + p_0\Delta V = Q. \tag{4.18}$$

The heat exchanged by a system during a monobaric transformation is therefore the variation of the enthalpy (hence the greek name ϑάλπειν, *thalpein*, to heat).
- The Gibbs free energy can be interpreted as follows: Let a system evolve in contact with a heat bath of temperature T_0 and an external pressostat of pressure p_0. We seek to recover work W' other than that exerted by the pressostat. By writing $W = -p_0\Delta V + W'$, the first law gives $\Delta U = Q - p_0\Delta V + W'$, with $Q = -\,T_0\Delta S_{\text{therm}}$. It is assumed that in the initial and final states, the system is in equilibrium with the heat bath and the pressostat, therefore at temperature $T = T_0$ and pressure $p = p_0$. Then,

$$\begin{aligned}\Delta G &= \Delta U + \Delta(-\,TS + pV) = Q - p_0\Delta V + W' - T_0\Delta S + p_0\Delta V\\ &= W' - T_0(\Delta S_{\text{therm}} + \Delta S) = W' - T_0\Delta S_{\text{univ}} < W',\end{aligned}$$

It is assumed that the operator wants to recover work (and therefore that $W' < 0$). The above inequality places a limit on the work that can be recovered: $|W'| < -\Delta G$. Therefore, during a monothermal and monobaric transformation, the energy "that can be released" other than the work of the pressostat, in other words the releasable enthalpy of a system, is the variation of the Gibbs free energy or free enthalpy, hence its name.

One should be careful not to confuse the free energy $F = U - TS$ with the potential $\Phi = U - T_0S$ suitable for the study of a system in contact with a heat bath. Similarly, the Gibbs free energy $G = U - TS + pV$ should not be confused with the potential $\Phi = U - T_0S + p_0V$ adapted to the study of a system in contact with a heat bath and a volume reservoir:

- The state functions F, G and H, obtained by Legendre transformations, are used to conveniently manipulate the chosen variables. To each set of variables corresponds an appropriate state function, independent of the external environment (surroundings) of the system.

- The thermodynamic potential $\varPhi$ is chosen according to the external environment of the system and it serves to find the thermodynamic equilibrium of the latter. It is minimal with respect to any set of variables of the system.

4.2.3 Gibbs-Duhem relation

A homogeneous fluid is characterized by three variables: $U = U(S, V, n)$, and therefore $F = F(T, V, n)$ and $G = G(T, p, n)$. The differential of G is

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}n.$$

Here G (as well as U, S, F, ...) is assumed to be extensive; this is always the case except when dealing with some very particular problems such as surface tension problems.

The extensivity property means that if the size of the system is multiplied by λ (that is, if n is replaced by λn without changing T or p), then G is multiplied by λ: $G(\lambda n, T, p) = \lambda G(n, T, p)$. Specifically, by taking $\lambda = 1/n$, we find that $G(n, T, p) = ng(1, T, p)$. Comparing with the differential, we see that $g(1, T, p) = \mu(T, p)$ and, finally,

$$G(T, p, n) = n\mu(T, p).$$

This is Euler's equation. Taking the differential, we find that $n\mathrm{d}\mu = -S\,\mathrm{d}T + V\,\mathrm{d}p$ and so, dividing by n,

$$\mathrm{d}\mu = -s\,\mathrm{d}T + v\,\mathrm{d}p, \tag{4.19}$$

with $s = S/n$ and $v = V/n$ the entropy and the molar volume of the fluid, respectively. This is Gibbs-Duhem relation.

4.3 Calorimetric coefficients of a fluid

4.3.1 Definitions of calorimetric coefficients

The *calorimetric coefficients* make it possible to express the entropy variations of a system as a function of T and other given variables. During a reversible transformation where the heat exchanged by the system is given by $\delta Q_{\mathrm{rev}} = T\,\mathrm{d}S$, these coefficients make it possible to quantify heat exchange, hence their name.

We will present the calorimetric coefficients of a homogeneous fluid for a closed system. The number of moles n is fixed once and for all and we will not write the terms in $\mathrm{d}n$ in the thermodynamic identities. Two variables to describe the fluid remain and there is a choice in how to write the thermodynamic identity, see frame 4.3:

$$\begin{aligned} \mathrm{d}U &= T\,\mathrm{d}S - p\,\mathrm{d}V, &\qquad \mathrm{d}F &= -S\,\mathrm{d}T - p\,\mathrm{d}V, \\ \mathrm{d}H &= T\,\mathrm{d}S + V\,\mathrm{d}p, &\qquad \mathrm{d}G &= -S\,\mathrm{d}T + V\,\mathrm{d}p. \end{aligned} \tag{4.20}$$

Video 3

Frame 4.4 : Calorimetric coefficients

- If we choose to work with the variables $\{T, V\}$, we can write

$$\mathrm{d}S = \frac{C_V}{T}\mathrm{d}T + \frac{\ell}{T}\mathrm{d}V \quad \Longleftrightarrow \quad T\mathrm{d}S = C_V\,\mathrm{d}T + \ell\,\mathrm{d}V. \tag{4.21}$$

With the thermodynamic identity (4.20), we obtain

$$\mathrm{d}U = C_V\,\mathrm{d}T + (\ell - p)\,\mathrm{d}V, \tag{4.22}$$

and therefore

$$C_V = T\frac{\partial S}{\partial T}\bigg|_V = \frac{\partial U}{\partial T}\bigg|_V \quad \text{and} \quad \ell = T\frac{\partial S}{\partial V}\bigg|_T = p + \frac{\partial U}{\partial V}\bigg|_T. \tag{4.23}$$

- If we choose to work in the variables $\{T, p\}$, we can write

$$\mathrm{d}S = \frac{C_p}{T}\mathrm{d}T + \frac{h}{T}\mathrm{d}p \quad \Longleftrightarrow \quad T\mathrm{d}S = C_p\,\mathrm{d}T + h\,\mathrm{d}p. \tag{4.24}$$

With the thermodynamic identity (4.20), we obtain

$$\mathrm{d}H = C_p\,\mathrm{d}T + (h + V)\,\mathrm{d}p, \tag{4.25}$$

and therefore

$$C_p = T\frac{\partial S}{\partial T}\bigg|_p = \frac{\partial H}{\partial T}\bigg|_p \quad \text{and} \quad h = T\frac{\partial S}{\partial p}\bigg|_T = -V + \frac{\partial H}{\partial p}\bigg|_T. \tag{4.26}$$

The coefficients C_V and C_p are the heat capacities at constant volume and at constant pressure, respectively. The coefficients ℓ and h have no name.

Caution: in both cases, $\mathrm{d}S$ is a differential, but $T\,\mathrm{d}S = \delta Q_{\mathrm{rev}}$ is not.
For an *isochoric* ($\mathrm{d}V = 0$) transformation of the fluid, we have $\delta W = 0$ and (4.22) gives

$$\delta Q = \mathrm{d}U = C_V\,\mathrm{d}T, \qquad \Leftrightarrow \qquad Q = \Delta U = \int_{T_\mathrm{i}}^{T_\mathrm{f}} C_V\,\mathrm{d}T. \tag{4.27}$$

For an *isobaric* ($\mathrm{d}p = 0$) and quasistatic transformation of the fluid, we have $\delta W = -p\,\mathrm{d}V$, $\mathrm{d}H = \mathrm{d}U + p\,\mathrm{d}V = \delta Q$ and (4.25) gives

$$\delta Q = \mathrm{d}H = C_p\,\mathrm{d}T, \qquad \Leftrightarrow \qquad Q = \Delta H = \int_{T_\mathrm{i}}^{T_\mathrm{f}} C_p\,\mathrm{d}T. \tag{4.28}$$

Video 4

4.3.2 Clapeyron equations

Clapeyron equations are used to calculate the calorimetric coefficients from the equation of state $p(T, V)$. There are several ways to get to these equations, here only the most effective is presented, which is based on the following remark. Choosing a set of variables, it is wise to find the “good” state function, the one whose differential expresses the thermodynamic identity in the variables selected. Maxwell's equations written with this state function then lead to the simplest calculations.

C_V and ℓ as a function of (T, V)

We want to express $\ell = T\,\partial S/\partial V|_T$, see (4.23). According to (4.20), it is clear that the "good" state function is the free energy. The Maxwell equation associated with $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V$ gives

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial p}{\partial T}\right|_V,$$

from where we get immediately

$$\ell = T\left.\frac{\partial p}{\partial T}\right|_V, \tag{4.29}$$

which is Clapeyron's first equation. Then, writing that $\mathrm{d}S$ in (4.21) is a differential,

$$\left.\frac{\partial(C_V/T)}{\partial V}\right|_T = \left.\frac{\partial(\ell/T)}{\partial T}\right|_V \quad\Longrightarrow\quad \left.\frac{\partial C_V}{\partial V}\right|_T = T\left.\frac{\partial^2 p}{\partial T^2}\right|_V, \tag{4.30}$$

which is Clapeyron's second equation. Knowing the equation of state (relation between p, T and V) thus makes it possible to calculate the coefficient ℓ and to find the dependence of C_V with respect to the volume. For example, for the ideal gas, we find that $\ell = p$ and C_V does not depend on V, that is to say that C_V depends only on T.

C_p and h as a function of (T, p)

We want to express $h = T\,\partial S/\partial p|_T$, see (4.26). According to (4.20), it is clear that the "good" state function is the Gibbs free energy. The Maxwell equation associated with $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p$ gives

$$-\left.\frac{\partial S}{\partial p}\right|_T = \left.\frac{\partial V}{\partial T}\right|_V.$$

From where we obtain immediately

$$h = -T\left.\frac{\partial V}{\partial T}\right|_p, \tag{4.31}$$

which is Clapeyron's first equation. Then, writing that $\mathrm{d}S$ in (4.24) is a differential,

$$\left.\frac{\partial(C_p/T)}{\partial p}\right|_T = \left.\frac{\partial(h/T)}{\partial T}\right|_p \quad\Longrightarrow\quad \left.\frac{\partial C_p}{\partial p}\right|_T = -T\left.\frac{\partial^2 V}{\partial T^2}\right|_p, \tag{4.32}$$

which is Clapeyron's second equation. Knowing the equation of state $V(T, p)$ thus makes it possible to calculate the coefficient h and to find the dependence of C_p with respect to the pressure. For example, for the ideal gas, we find that $h = -V$ and that C_p depends only on T.

4.3.3 Relationships between coefficients

There are many relations between all the coefficients that we have just defined; in this section we present the main ones.

Relationship between thermoelastic and calorimetric coefficients

Recall the following definitions:

Frame 4.5 : Thermoelastic coefficients

For a homogeneous fluid, the following coefficients are defined:

- The isothermal compressibility coefficient

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial p}\bigg|_T \qquad \text{in Pa}^{-1},$$

  which indicates how easy or difficult it is to compress the fluid by increasing the pressure. χ_T is an intensive quantity that is always positive.
- The thermal expansion coefficient

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_p \qquad \text{in K}^{-1},$$

  which indicates how the volume changes with temperature. α is an intensive quantity which is generally positive, but not always. (For example, if we extend the definition of α to isotropic solids, then the α of rubber is negative.)

For example, for the ideal gas, we have $\chi_T = 1/p$ and $\alpha = 1/T$.

We also sometimes define the coefficient

$$\beta = \frac{1}{p}\frac{\partial p}{\partial T}\bigg|_V,$$

but this coefficient is redundant. Indeed, since p, T and V are connected by the equation of state, we must have

$$\frac{\partial V}{\partial p}\bigg|_T \times \frac{\partial p}{\partial T}\bigg|_V \times \frac{\partial T}{\partial V}\bigg|_p = -1.$$

(General mathematical property valid as soon as three quantities are connected to each other). We can deduce that

$$\alpha = \beta p \chi_T.$$

Comparing these definitions to the Clapeyron relations (4.29) and (4.31), we immediately have

$$\ell = \beta T p = \frac{\alpha T}{\chi_T} \qquad \text{and} \qquad h = -\alpha T V. \tag{4.33}$$

In particular,

$$\frac{h}{\ell} = -V\chi_T = \frac{\partial V}{\partial p}\bigg|_T. \tag{4.34}$$

Video 5

Mayer's relation

Mayer's relation is the relationship between the two heat capacities that have been defined, at constant volume C_V and at constant pressure C_p. Substituting the differential of the volume

$$\mathrm{d}V = \left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial V}{\partial p}\right|_T \mathrm{d}p$$

in relation (4.21), we get

$$T\mathrm{d}S = C_V\mathrm{d}T + \ell\left[\left.\frac{\partial V}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial V}{\partial p}\right|_T \mathrm{d}p\right] = \left[C_V + \ell\left.\frac{\partial V}{\partial T}\right|_p\right]\mathrm{d}T + \ell\left.\frac{\partial V}{\partial p}\right|_T \mathrm{d}p.$$

Compared with the definition (4.24), we find (4.34) and we obtain

$$C_p - C_V = \ell\left.\frac{\partial V}{\partial T}\right|_p = \alpha V\ell. \tag{4.35a}$$

Using (4.33), we also arrive at

$$C_p - C_V = \frac{\alpha^2 TV}{\chi_T} = \frac{T}{V\chi_T}\left(\left.\frac{\partial V}{\partial T}\right|_p\right)^2. \tag{4.35b}$$

These two expressions of $C_p - C_V$ are equivalent formulations of Mayer's relation. The expression (4.35b) will find its utility after the derivation of thermodynamic inequalities (paragraph 4.3.5). The ratio of the heat capacities is defined as:

$$\gamma = \frac{C_p}{C_V}, \tag{4.36}$$

which is a dimensionless number taking, as we will see, simple values for most fluids. Taking for example Mayer's relation (4.35a), the ratio γ allows to express

$$C_V = \frac{1}{\gamma - 1}\alpha V\ell \qquad \text{and} \qquad C_p = \frac{\gamma}{\gamma - 1}\alpha V\ell. \tag{4.37}$$

4.3.4 Isentropic coefficients

Video 6

In addition to the isochoric, isobaric or isothermal transformations, there are isentropic transformations, that is to say with constant entropy. It suffices, for example, to carry out an adiabatic transformation during which the fluid receives work quasistatically: then, according to the adiabatic theorem, the transformation is reversible and isentropic ($S = S_{\text{univ}} = \text{cste}$).

In parallel to the isothermal compressibility, we define the *isentropic compressibility* (or adiabatic compressibility)

$$\chi_S = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_S. \tag{4.38}$$

As explained in a video, this coefficient χ_S is part of the expression for the velocity of sound in a fluid.

Video 7

The ratio of the two compressibilities can be calculated. For a quasistatic and isentropic transformation, we have

$$T\,\mathrm{d}S = C_V\,\mathrm{d}T + \ell\,\mathrm{d}V = C_p\,\mathrm{d}T + h\,\mathrm{d}p = 0$$

and thus

$$\mathrm{d}T = -\frac{\ell}{C_V}\mathrm{d}V = -\frac{h}{C_p}\mathrm{d}p \quad\Longrightarrow\quad \left.\frac{\partial V}{\partial p}\right|_S = \frac{C_V}{C_p}\frac{h}{\ell} = -\frac{C_V}{C_p}V\chi_T,$$

where we used (4.34). With the definition (4.36) of γ, we finally obtain

$$\frac{\chi_T}{\chi_S} = \frac{C_p}{C_V} = \gamma, \tag{4.39}$$

which is Reech's formula.

Video 8

4.3.5 Thermodynamic inequalities

We consider here a fluid in contact with a heat bath at temperature T_0 and a volume reservoir at pressure p_0. It was shown in section 4.1 that the potential $\Phi = U - T_0 S + p_0 V$ was minimal at equilibrium. Using $\mathrm{d}\Phi = 0$, we showed that equilibrium was characterized by $T = T_0$ and $p = p_0$. However, the condition $\mathrm{d}\Phi = 0$ is not sufficient to characterize a minimum.

By writing that Φ is indeed a local minimum at equilibrium, we will obtain inequalities on the thermodynamic coefficients.

We choose here to work with variables V and T (other choices are possible and lead to the same results). At equilibrium, $T = T_0$ and $V = V_{\mathrm{eq}}$ (which is the volume such that $p = p_0$). We place ourselves at a point $(T_0 + t, V_{\mathrm{eq}} + v)$ close to equilibrium (t and v are small); then a development to the second order gives

$$\Phi(T_0+t, V_{\mathrm{eq}}+v) = \Phi(T_0, V_{\mathrm{eq}}) + \frac{1}{2}\left[\left.\frac{\partial^2\Phi}{\partial T^2}\right|_V t^2 + 2\frac{\partial^2\Phi}{\partial T\partial V}tv + \left.\frac{\partial^2\Phi}{\partial V^2}\right|_T v^2\right] + \cdots \tag{4.40}$$

By implication, the three second derivatives are evaluated at (T_0, V_{eq}). The terms of first order are null: that is how we found T_0 and V_{eq}. Higher order terms are negligible when t and v tend to 0.

The minimum of Φ is reached at (T_0, V_{eq}) if for all t and v we have $\Phi(T_0+t, V_{\mathrm{eq}}+v) \geq \Phi(T_0, V_{\mathrm{eq}})$. Taking t and v small, we find that the term in brackets in (4.40) must be positive. In particular, taking successively $v = 0$ and $t = 0$, we find that we necessarily have

$$\text{at point } (T_0, V_{\mathrm{eq}}) \qquad \left.\frac{\partial^2\Phi}{\partial T^2}\right|_V \geq 0 \qquad \text{and} \qquad \left.\frac{\partial^2\Phi}{\partial V^2}\right|_T \geq 0 \tag{4.41}$$

(In general, condition (4.41) is necessary but not sufficient to ensure that the term in brackets in (4.40) is positive.)

It only remains to calculate the derivatives; first in V:

$$\left.\frac{\partial\Phi}{\partial V}\right|_T = \left.\frac{\partial U}{\partial V}\right|_T - T_0\left.\frac{\partial S}{\partial V}\right|_T + p_0 = (\ell - p) - T_0\frac{\ell}{T} + p_0 = \left(1 - \frac{T_0}{T}\right)\ell - p + p_0$$

and

$$\left.\frac{\partial^2\Phi}{\partial V^2}\right|_T = \left(1 - \frac{T_0}{T}\right)\left.\frac{\partial\ell}{\partial V}\right|_T - \left.\frac{\partial p}{\partial V}\right|_T = \left(1 - \frac{T_0}{T}\right)\left.\frac{\partial\ell}{\partial V}\right|_T + \frac{1}{V\chi_T}.$$

And then in T:

$$\left.\frac{\partial\Phi}{\partial T}\right|_V = \left.\frac{\partial U}{\partial T}\right|_V - T_0\left.\frac{\partial S}{\partial T}\right|_V = C_V - T_0\frac{C_V}{T} = \left(1 - \frac{T_0}{T}\right)C_V$$

and

$$\left.\frac{\partial^2 \Phi}{\partial T^2}\right|_V = \left(1 - \frac{T_0}{T}\right)\left.\frac{\partial C_V}{\partial T}\right|_V + \frac{T_0}{T^2} C_V.$$

The condition (4.41) then becomes $C_V/T_0 \geq 0$ and $1/(V_{\mathrm{eq}}\chi_T) \geq 0$ or, more simply,

$$C_V \geq 0 \qquad \text{et} \qquad \chi_T \geq 0.$$

The expression (4.35b) of the Mayer's relation shows that

$$C_p \geq C_V \geq 0 \tag{4.42}$$

and so $\gamma = \dfrac{C_p}{C_V} \geq 1$. Reech's formula then shows that

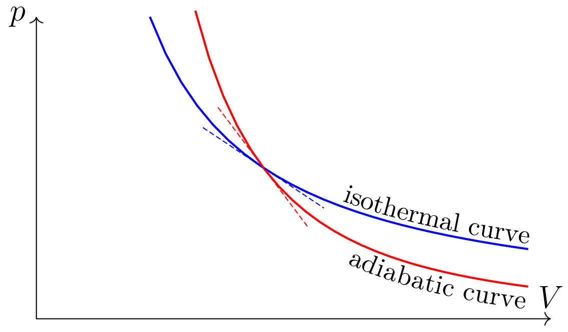
$$\chi_T \geq \chi_S \geq 0. \tag{4.43}$$

The two sets of relations (4.42) and (4.43) constitute the thermodynamic inequalities of the fluid. They lead immediately to the following applications.

- Consider a transformation where the fluid receives a quantity of heat $Q > 0$. Suppose, for convenience, that the heat capacities C_V and C_p are constant. If the transformation is isochoric, the temperature rise ΔT_V is given by (4.27): $\Delta T_V = \Delta U/C_V = Q/C_V$. If the transformation is monobaric (or isobaric), the temperature rise ΔT_p is given by (4.28): $\Delta T_p = \Delta H/C_p = Q/C_p$. According to the inequality (4.42), we have $\Delta T_V \geq \Delta T_p$: the isochoric increase in temperature is higher than the isobaric increase.
- By definition of the compressibilities, inequality (4.43) imposes

  $$\left.\frac{\partial p}{\partial V}\right|_S \leq \left.\frac{\partial p}{\partial V}\right|_T \leq 0.$$

  In the Clapeyron diagram (V, p), the slopes of the isothermal and adiabatic curves are therefore negative and, in absolute value, the slope of the adiabatic is larger than the slope of the isotherm. According to Reech's formula (4.39), the ratio of the two slopes is given by the coefficient $\gamma \geq 1$.



Comparison of isothermal and adiabatic curves in the Clapeyron diagram.

Chapter 5

Video 1

Microcanonical statistical mechanics

5.1 The postulate of statistical mechanics

The fundamental ideas of statistical mechanics, already described in section 5, are recalled:

- The **macrostate** of a system is its macroscopic description, using a limited number of variables. For example, two different glasses of water at equilibrium with the same temperature, the same pressure and the same volume are in the same macrostate.
- The **microstate** of a system is its exhaustive microscopic description: it means giving the position, the velocity, the orientation, *etc.*, of each molecules within the system. Thus, the two glasses of water of the preceding example are certainly in different microstates.
- A mechanical, deterministic description of the system would be to follow its microstate as a function of time, which is impossible in practice.
- We are therefore led to follow a **probabilistic approach**: for a given macrostate, we work with the probabilities of each of the compatible microstates.

The starting point of statistical mechanics is to postulate the probabilities of microstates, see also frame 5 and the video:

Video 2

Frame 5.1 : **Postulate of statistical mechanics**

We consider an *isolated* system, and we write

$$\Omega = \begin{bmatrix} \text{The number of microstates accessible} \\ \text{to the system given its macrostate} \end{bmatrix}.$$

Then:

- at thermodynamic equilibrium, all these microstates are equiprobable,
- the entropy of the system is given by

$$S = k_B \ln \Omega.$$

Remarks:

- For the simple examples that we discuss in this chapter, Ω is a finite number, and the formula $S = k_B \ln \Omega$ is naturally interpreted.
- If one wants to treat the ideal gas classically, describing a microstate consists in giving the position and impulse of each of the particles constituting the gas. We then have

a problem: since there is an infinity of possible positions, Ω is infinite. We overcome this by supposing that positions and impulses are known only with a given precision, small but not null; there is then a finite number of positions and Ω is finite. Of course, the expressions of Ω and S then depend on the selected precisions, but the entropy variations ΔS between two states do not.

- In reality, classical mechanics is only an approximation. In a quantum approach, the number of microstates Ω must be understood as the number of eigenstates of the Hamiltonian. It is a finite number that depends on Planck's constant h.

5.2 The lattice gas

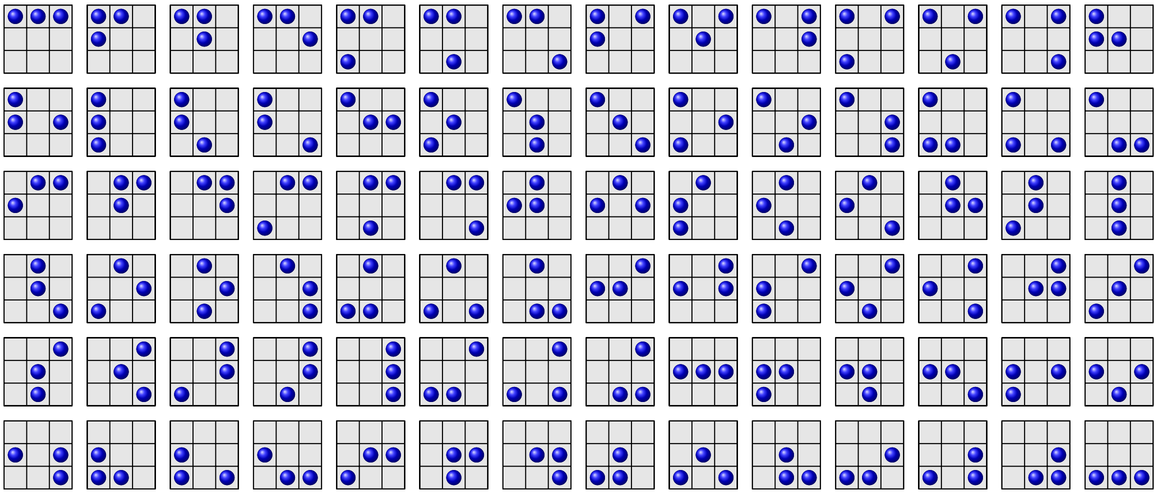
To understand how the postulate of statistical mechanics works, we consider in this section the simplest possible system.

In this system, a macrostate depends only on two parameters, the number of particles N and the volume V (there is no energy!). From a microscopic point of view, we suppose that the system consists of αV boxes (we suppose that this number is an integer). Each box can accommodate at most one particle. Then α is the number of boxes available per m^3. Describing a microstate therefore consists in giving the list of the N occupied boxes.

We want to calculate Ω.

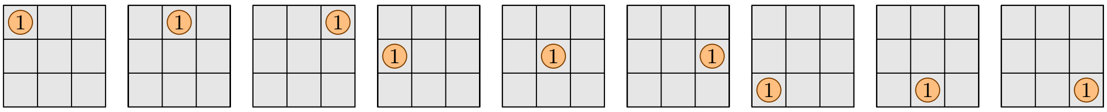
5.2.1 Calculation of the number of microstates

To take an example, with $N = 3$ and $\alpha V = 9$, there are $\Omega = 84$ different microstates:

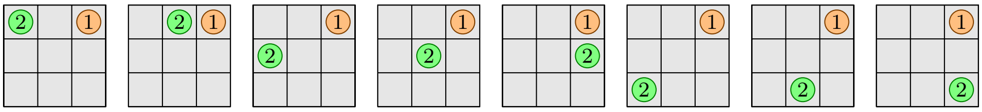


This number 84 is calculated as follows: we start by assuming that the particles are numbered: ①, ② and ③.

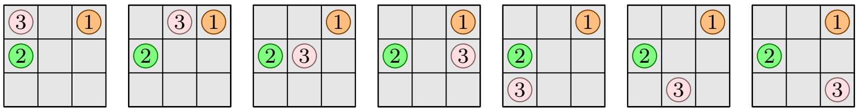
To place particle ①, there are nine possibilities:



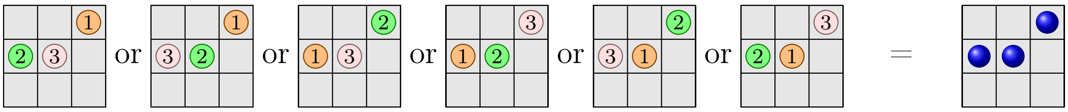
For each of these nine possibilities, there are eight ways to place particle ②. For example, starting from the third choice above, we have:



So there are $9 \times 8 = 72$ ways to place particles ① and ②. For each of these choices, there are seven ways to place particle ③. For example, starting from the third choice above, we have:



So there are $9 \times 8 \times 7 = 504$ ways to place particles ①, ② and ③. But this number is not Ω; indeed, in the initial problem, the particles are not numbered, they are indistinguishable, and the six following configurations represent in fact the same microstate:



The effect of numbering the balls was therefore to count each microstate six times. This overestimate is corrected by dividing our result by 6, where $6 = 3! = 3 \times 2 \times 1$ is the number of permutations of {①, ②, ③}, *i.e.* the number of orders in which these three elements can be listed. We finally find:

$$\Omega = \frac{9 \times 8 \times 7}{6} = 84.$$

Now generalising this result to any N and αV, we find

$$\Omega(N, V) = \frac{\overbrace{\alpha V \times (\alpha V - 1) \times (\alpha V - 2) \times \cdots \times (\alpha V - N + 1)}^{N \text{ terms}}}{N!}.$$

The numerator is the number of ways to arrange N *labelled* particles in αV boxes. As the particles are, in fact, indistinguishable, the overestimate is corrected by dividing by $N! = N \times (N - 1) \times \cdots \times 2 \times 1$, which is the number of possible permutations of N elements.

Multiply by $(\alpha V - N)!$ the numerator and the denominator, we form $(\alpha V)!$ in the numerator and we get

$$\Omega(N, V) = \frac{(\alpha V)!}{N!(\alpha V - N)!} = \binom{\alpha V}{N}. \tag{5.1}$$

The number $\binom{\alpha V}{N}$ is a *binomial coefficient* and reads "αV choose N." It represents the number of ways to choose N objects (here the boxes) among αV. The binomial coefficients are the numbers that appear in Pascal's triangle, and also in Newton's binomial formula:

$$(a + b)^n = \sum_{p=0}^{n} \binom{n}{p} a^p\, b^{n-p}.$$

In the last century, in France, the notation of this binomial coefficient was $\mathrm{C}_n^p = \binom{n}{p}$, with the indices interchanged.

5.2.2 Stirling's approximation

To be able to consider the lattice gas configuration as a thermodynamic system, one needs to calculate (5.1) for large values of N and αV. Stirling's formula gives an equivalent for $N!$ and for $\ln(N!)$ when N is large.

Frame 5.2: **Stirling's approximation**

Asymptotically, for N large, we have

$$N! \sim \sqrt{2\pi N} N^N e^{-N}, \tag{5.2}$$

and thus

$$\ln(N!) \sim N \ln N - N. \tag{5.3}$$

Remarks:

- This formula is due to James Stirling, an 18th century Scottish mathematician, not to be confused with Robert Stirling, Scottish himself, and inventor of the "Stirling Engine" in the 19th century.
- We obtain (5.3) by taking the logarithm of (5.2) and neglecting the term $\ln \sqrt{2\pi N}$. This term is indeed negligible: for $N = 10^{20}$, we have $N \ln N \approx 46\,10^{20}$ and $\ln \sqrt{2\pi N} \approx 24$.
- The approximations (5.2) and (5.3) are very good:

N	$N!$	$\sqrt{2\pi N} N^N e^{-N}$	$\ln(N!)$	$N \ln N - N$
100	$9.333\,10^{157}$	$9.325\,10^{157}$	363.7	360.5
1000	$4.0239\,10^{2567}$	$4.0235\,10^{2567}$	5912	5908
1 000 000	$8.263932\,10^{5\,565\,708}$	$8.263931\,10^{5\,565\,708}$	$1.281552\,10^7$	$1.281551\,10^7$

Here is a quick argument to obtain (5.3). (Getting (5.2) would require a little more work...)

$$\begin{aligned} \ln(N!) &= \ln\Big(N \times (N-1) \times (N-2) \times \ldots \times (N - [N-1])\Big) \\ &= \ln N + \ln(N-1) + \ln(N-2) + \cdots + \ln(N - [N-1]). \end{aligned}$$

Using $\ln(N-k) = \ln N + \ln\left(1 - \frac{k}{N}\right)$, we obtain

$$\begin{aligned} \ln(N!) &= N \ln N + \left[\ln\left(1 - \frac{1}{N}\right) + \ln\left(1 - \frac{2}{N}\right) + \cdots + \ln\left(1 - \frac{N-1}{N}\right)\right] \\ &\approx N \ln N + N \int_0^1 \mathrm{d}x \, \ln(1-x) \end{aligned}$$

where the sum between square brackets is the usual approximation of an integral by a discrete sum taken over a large number of very close values. The calculation of the integral gives the result.

5.2.3 Lattice gas entropy and pressure

We are now able to calculate the entropy of our system:

$$\begin{aligned} S = k_B \ln \Omega = k_B \ln \frac{(\alpha V)!}{N!(\alpha V - N)!} &= k_B \Big[\ln[(\alpha V)!] - \ln[N!] - \ln[(\alpha V - N)!]\Big] \\ = k_B \Big[\alpha V \ln(\alpha V) - (\alpha V) - [N \ln N - N] &- [(\alpha V - N) \ln(\alpha V - N) - (\alpha V - N)]\Big], \end{aligned}$$

where Stirling's formula was used three times. The terms without logarithm simplify, and we finally obtain:

$$S = k_B \Big[\alpha V \ln(\alpha V) - N \ln N - (\alpha V - N)\ln(\alpha V - N)\Big]. \tag{5.4}$$

For this very simple system without energy, we can do little thermodynamics. We can still calculate the pressure:

$$\frac{p}{T} = \frac{\partial S}{\partial V} = k_B \Big[\alpha \ln(\alpha V) + \alpha - \alpha \ln(\alpha V - N) - \alpha\Big] = -\alpha k_B \ln \frac{\alpha V - N}{\alpha V} = -\alpha k_B \ln\Big[1 - \frac{N}{\alpha V}\Big].$$

We note in particular that if we take the limit $\alpha \to \infty$, we obtain the ideal gas equation:

$$\frac{p}{T} = k_B \frac{N}{V}. \tag{5.5}$$

It is not surprising to recover an ideal gas: if $\alpha \to \infty$, *i.e.* if the number of available cells per unit volume diverges, the system becomes similar to a system where the particles have continuous positions and do not interact, that is, an ideal gas. What is remarkable is that it is possible to easily find this empirical law of thermodynamics only from the Boltzmann postulate, $S = k_B \ln \Omega$.

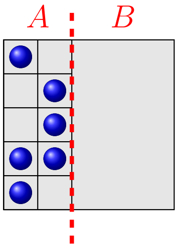
(In fact, it is difficult to speak of temperature in a system without energy. To complete the calculation, it would be necessary to take into account the kinetic energy of the particles. One would find that Ω is multiplied by a function of E and N (but not of V!) and the expression of p/T would be unchanged.)

5.2.4 Probability of a microscopic state of part of a system

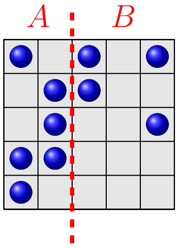
A lattice gas of N particles is still considered in a volume V, isolated from the surroundings. The number of microstates is $\Omega(N, V)$ and, by postulate, all these microstates are equiprobable. Therefore the probability of one state is $1/\Omega(N, V)$.

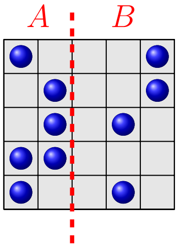
The system is virtually cut into two parts of volumes V_A (left) and V_B (right), with $V = V_A + V_B$. Subsystem A is not isolated, the Boltzmann postulate cannot be applied directly. Nevertheless, we try to determine the probability of a given configuration of system A.

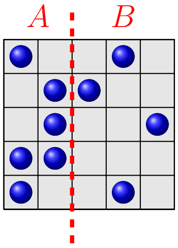
To get an idea, we take $\alpha V = 25$, $\alpha V_A = 10$, $\alpha V_B = 15$ and $N = 10$. We are looking for the probability that the subsystem A has the following microstate σ_A:

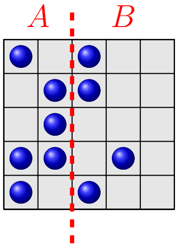


If we consider the complete system, there are many microstates compatible with σ_A. Here are four:









For the complete system, there are in total $\Omega(N, V) = \binom{25}{10} = 3\,268\,760$ microstates. Of these microstates, there are only $\Omega(N - N_A, V_B) = \binom{15}{4} = 1365$ for which A is in a given state σ_A; it corresponds to the number of ways the remaining particles (here, there are four) can be arranged in the fifteen cells of part B. Using the postulate of equiprobability, one deduces that the probability of observing the given σ_A state is $1365/3\,268\,760 \approx 0.04\,\%$.

In general, we have

$$\mathrm{Proba}(\sigma_A) = \frac{\Omega(N - N_A, V_B)}{\Omega(N, V)}, \tag{5.6}$$

where N_A depends on σ_A: it is the number of particles present in the subsystem A when it is in the state σ_A. This expression is understood as (number of favorable cases)/(total number of cases).

Note that the microstates of A are not equiprobable! The probability of being in the state σ_A depends on the number of particles N_A for the microstate σ_A.

5.2.5 Probability of a macroscopic state of part of a system

Equation (5.6) gives the probability of the microscopic state of part A. We are now interested in the number of particles N_A in part A; this number N_A characterises the macroscopic state of A. For a given value of N_A, all the microstates of part A having this number of particles have the same probability (5.6). Moreover, there are $\Omega(N_A, V_A)$ microstates with N_A particles in A. We deduce that

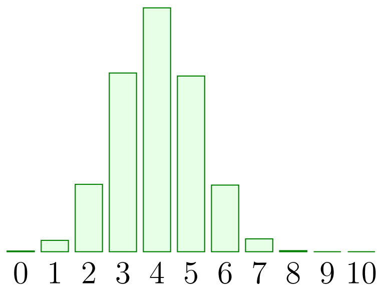
$$\mathrm{Proba}(N_A) = \frac{\Omega(N_A, V_A)\Omega(N - N_A, V_B)}{\Omega(N, V)}. \tag{5.7}$$

Do not confuse the following quantities:

- $\mathrm{Proba}(\sigma_A)$ is the probability of observing a given microstate σ_A. It depends only on N_A, the number of particles in A for this microstate.
- $\mathrm{Proba}(N_A)$ is the probability that there are N_A particles in A. So this is the probability that A is in either one of the microstates with N_A particles.

With expression (5.1) of $\Omega(N, V)$, we can calculate the probabilities (5.7) for the values in the example ($\alpha V_A = 10$, $\alpha V_B = 15$, $N = 10$). We find

$\mathrm{Proba}(N_A = 0) = 9.2\,10^{-4}\,\%$ $\quad$ $\mathrm{Proba}(N_A = 1) = 1.5\,\%$
$\mathrm{Proba}(N_A = 2) = 8.9\,\%$ $\quad$ $\mathrm{Proba}(N_A = 3) = 23.6\,\%$
$\mathrm{Proba}(N_A = 4) = 32.2\,\%$ $\quad$ $\mathrm{Proba}(N_A = 5) = 23.2\,\%$
$\mathrm{Proba}(N_A = 6) = 8.8\,\%$ $\quad$ $\mathrm{Proba}(N_A = 7) = 1.7\,\%$
$\mathrm{Proba}(N_A = 8) = 1.4\,10^{-3}\,\%$ $\quad$ $\mathrm{Proba}(N_A = 9) = 4.6\,10^{-5}\,\%$
$\mathrm{Proba}(N_A = 10) = 3\,10^{-7}\,\%$



5.2.6 Irreversibility and fluctuations

Imagine an experiment where, initially, we force the ten particles of our example to fill the ten boxes of part A. At a given moment, we lift this constraint (we allow the particles to move). After a time long enough for the system to reach thermodynamic equilibrium, we measure the number N_A of particles in A. This number is random with the probabilities just given.

In particular, the probability of returning to the initial state ($N_A = 10$) is already very low, equal to $3\,10^{-7}\,\%$. For a system ten times larger ($N = 100$, $\alpha V_A = 100$, $\alpha V_B = 150$), this probability becomes $\mathrm{Proba}(N_A = 100) = 3.3\,10^{-32}\,\%$. For thermodynamic systems (N is of the order of the Avogadro constant), the probability to go back to the initial configuration is unimaginably small. This is a manifestation of irreversibility, already discussed in section 5, and illustrated by a video.

Video 3

From expression (5.7), the properties of the random variable N_A for large systems can be calculated. We want to consider the following physical situation: in a room at 20°C and 1 atm, consider a volume of air $V_A = 1\,\ell$. What is the number of particles N_A (diazote, dioxygen, ...) inside?

In thermodynamics, we would make the following reasoning: throughout the room, the particle density is

$$\frac{N}{V} = \frac{p}{k_B T} = 2.5\,10^{25}\,\text{particles/m}^3 \tag{5.8}$$

Therefore in one liter, there are

$$N_A = 2.5\,10^{25} \times 10^{-3} = 2.5\,10^{22}\,\text{particles}, \tag{5.9}$$

or an amount of substance $n_A = 42\,\text{mmol}$, which has a mass $m_A = 1.2\,\text{g}$.

In statistical mechanics, the variable N_A is random and its properties are calculated from (5.7). It is a rather complicated calculation, which begins by taking the limit $\alpha \to \infty$ (to have an ideal gas in the continuum), then the limit $N \to \infty$ and $V \to \infty$ with the N/V ratio fixed and given by (5.8) (because the room has a volume large with respect to $1\,\ell$). At the end of this calculation (not part of this course), one arrives at the following results:

- The average value of N_A is given by the result (5.9) of thermodynamics.
- The fluctuations of N_A around its mean value are described by a normal distribution (a Gaussian) characterised by a standard deviation equal to $\sqrt{N_A}$. This is **the law of large numbers**.

We can write

$$N_A = (2.5\,10^{22} \pm 1.6\,10^{11})\,\text{particles}. \tag{5.10}$$

These fluctuations, although large in absolute value, are negligible compared to the average value of N_A. Moreover, if we now express the amount of substance and the mass in our system, we obtain

$$n_A = (42 \pm 2.6\,10^{-10})\,\text{mmol}, \qquad m_A = (1.2 \pm 7.6\,10^{-12})\,\text{g}. \tag{5.11}$$

It is almost impossible to measure these fluctuations, and the theory of thermodynamics is well justified for such large systems. However, if one considers a volume $V_A = 1\,\mu\text{m}^3$ or smaller, the effect of the fluctuations begin to show.

Video 4

5.3 Two-level systems

Video 5

Let us finish this chapter by studying two very simple systems. One, Langmuir's model is presented in a video. The other is the two-level system. An isolated system consisting of N fixed particles is considered (for example, these are the atoms of a solid). It is assumed that these particles can be in two states:

- the fundamental, of 0 energy,
- the excited state, with energy $\epsilon > 0$,

and we neglect the interaction energy between particles. For example, a paramagnetic metal immersed in a magnetic field $\vec{B}$ can be seen as a two-level system. Each atom has a magnetic moment; in the fundamental state, this moment is aligned with the field $\vec{B}$ and in the excited state it is opposite to $\vec{B}$.

We want to determine the number $\Omega(N, U)$ of microstates for a macrostate characterised by its number of particles N and its energy U.

The possible values of the energy U of the system are 0, ϵ, 2ϵ, 3ϵ, …, $N\epsilon$: the system has the energy $U = M\epsilon$ when M particles are in the excited state and $N - M$ in the fundamental.

There is only one microstate of zero energy (all the particles being in the fundamental state). There are N microstates of energy ϵ (there is only one excited particle, but it can be any one in the system).

Generally $\Omega(N, U)$ is given by the number of ways to choose the U/ϵ excited particles in the system. This Ω is given by a binomial, as in the previous section:

$$\Omega(N, U) = \binom{N}{U/\epsilon}, \tag{5.12}$$

to be compared to (5.1).

From there, all the calculations are similar to those in the previous section, and only a few results will be given hereafter. We compute the entropy $S = k_B \ln \Omega$ as before, with the help of Stirling's formula, and we find

$$S = k_B \Big[N \ln N - \frac{U}{\epsilon} \ln \frac{U}{\epsilon} - \Big(N - \frac{U}{\epsilon} \Big) \ln \Big(N - \frac{U}{\epsilon} \Big) \Big], \tag{5.13}$$

to be compared to (5.4).

From the entropy, we can obtain the temperature $T(N, U)$ of the system

$$\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{k_B}{\epsilon} \ln \frac{N\epsilon - U}{U}. \tag{5.14}$$

We can then inverse this relation to get the internal energy $U(N, T)$ of the system, then calculate the heat capacity $C = \partial U / \partial T$, *etc.* In the case where the two-level system is a magnetic system, one can also determine the magnetisation of the system as a function of the temperature and obtain Curie's formula: in the limit of weak $\vec{B}$ fields and high temperatures T, the magnetisation is proportional to $\vec{B}/T$.

5.4 Summary

To microcanonically study a system, the procedure to follow is always the same:

Frame 5.3 : Procedure to follow

For a given system,

- Calculate the number of microstates $\varOmega$ according to the macroscopic variables (U, V, N, *etc.*). This calculation involves combinatorial problems and, very often, binomials and factorials appear.
- Calculate the entropy $S = k_B \ln \varOmega$. Stirling's formula is often used.
- Calculate the thermodynamic parameters. Using the thermodynamic identity $\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V - \frac{\mu}{T}\mathrm{d}N + \cdots$, we can calculate T, p, μ, *etc.* by deriving the entropy with respect to its parameters.
- In the previous step, we calculated $T(U, V, N, \ldots)$. By inverting this relation, we obtain $U(T, V, N, \ldots)$, which is more practical. We can then calculate other thermodynamic quantities such as the thermal capacity $C_V = \partial U/\partial T$.

Note: in statistical mechanics, the number of particles N rather than the number of moles n, is used more readily. The chemical potential is then defined as $\mu = -T\frac{\partial S}{\partial N}$, and not as $\mu = -T\frac{\partial S}{\partial n}$ in thermodynamics. The μ of statistical mechanics is equal to the μ of thermodynamics divided by the Avogadro constant $\mathcal{N}_A$.

The statistical approach makes it possible to highlight the existence of fluctuations:

Frame 5.4 : Fluctuations in Statistical Mechanics

We consider an isolated system that is divided into two parts A and B. For any thermodynamic quantity X (the number of particles, energy, *etc.*), we are interested in the value X_A of this quantity in part A. Then

- The quantity X_A is random, and its distribution is described by a Gaussian.
- The average value of X_A is equal to the prediction of Thermodynamics.
- Moreover assuming that part A is much smaller than part B, the fluctuations of X_A are typically equal to its mean value divided by $\sqrt{N_A}$; it is the law of large numbers.

The significance of the last point is that if part A contains $N_A = 10^{20}$ particles, the quantity X_A and its mean value are the same over ten significant digits.

Chapter 6

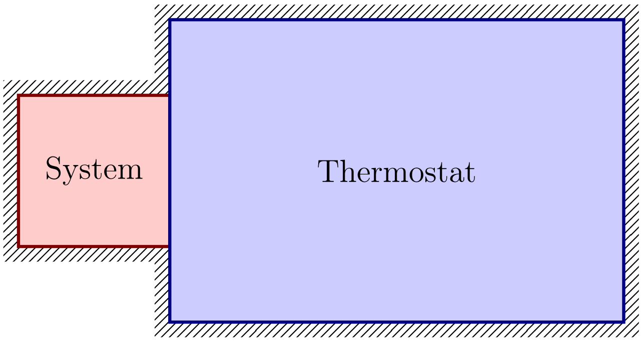
Video 1

Canonical statistical mechanics

6.1 The canonical ensemble

6.1.1 Positioning the problem

In the previous chapter, we introduced Boltzmann's postulate, see frame 5.1, which allows us to calculate the entropy of an isolated system, and therefore, to study its thermodynamic properties. However, this postulate only applies to isolated systems. The purpose of the canonical description is to directly determine the thermodynamic properties of a system in contact with a thermostat.



A thermostat is an ideal system, considered so big that its temperature does not change, even when it receives (or gives) energy in the form of heat (see frame 3.4). In particular, the thermostat imposes its temperature on the system. We consider that the system can only exchange heat with the thermostat, and the {system + thermostat} entity is isolated.

The object of interest is the system, and we want to describe the microstates *of the system* (and not those of the thermostat). As the system is not isolated, its energy can fluctuate and all the microstates, *whatever their energy*, can be observed. (In contrast, in a microcanonical description, the energy of the system has a set value, and only these microstates with that specific energy can be observed.)

The microstates of the system are indexed by the letter σ, and we use the following notations:

$$\text{For a given microstate } \sigma\text{:} \begin{cases} E_\sigma & \text{the energy of the system when it is in the microstate } \sigma, \\ P_\sigma & \text{the probability that the system is in the microstate } \sigma. \end{cases}$$

6.1.2 Boltzmann's factor

The fundamental result, which will be demonstrated at the end of this chapter, is as follows:

Video 2

Frame 6.1 : Boltzmann's factor

For a system at thermodynamic equilibrium in contact with a thermostat at temperature T,

$$P_\sigma \text{ is proportional to } \exp\left(-\frac{E_\sigma}{k_B T}\right). \tag{6.1}$$

Remarks:

- The expression (6.1) is of course valid for a thermodynamic system consisting of a large number of particles. Surprisingly, it remains valid for a system composed of a small number of particles, or even a single particle!
- In expression (8.1), the thermostat intervenes only via its temperature T; the way it is built has no influence on the statistics of the system.
- For a *quantum* system, the microstates we consider are, as in microcanonics, the eigenstates of the Hamiltonian. They form a discrete set and we can define the probability (6.1) of each of these states.
- For a *classical* system, all the microstates are *continuous*. It is then necessary to replace the probability P_σ by a probability density; see section 6.2.6 for more details.
- In statistical mechanics, the inverse temperature

  $$\beta = \frac{1}{k_B T}$$

  is often introduced to simplify the notations.
- The proportionality factor is often denoted $\frac{1}{Z}$, where Z is called the *partition function*. Equation (6.1) is then written as

  $$P_\sigma = \frac{1}{Z} e^{-\beta E_\sigma}.$$

  The partition function depends on the temperature T of the thermostat and the properties of the system, but of course, *it does not depend on* σ.

6.2 Applications

Video 3

6.2.1 Two-level systems

The simplest system one can study in statistical physics is the two-level system (or two-state system), which is a system where there are only two distinct microstates. For example, these two levels may be the two possible orientations of the angular momentum along the z axis for a particle with spin 1/2, or the symmetric and antisymmetric states of an ammonia (NH_3) molecule, *etc.* According to the system being considered, we can note these two levels $\{\uparrow, \downarrow\}$, $\{+, -\}$, or $\{A, S\}$, *etc.* Here, we decide to simply note them $\{1, 2\}$:

$$\sigma \in \{1, 2\}.$$

We will therefore refer to E_1, the energy of the system in state $\sigma = 1$, and E_2, the energy of the system in state $\sigma = 2$. The probabilities of the two states are denoted P_1 and P_2.

It is assumed that the system is in equilibrium with a thermostat at temperature T. According to (6.1), with $1/Z$ the proportionality factor and $\beta = 1/(k_B T)$, we have

$$P_1 = \frac{1}{Z} e^{-\beta E_1}, \qquad P_2 = \frac{1}{Z} e^{-\beta E_2}. \tag{6.2}$$

Z is determined by normalisation of the probabilities:

$$P_1 + P_2 = 1, \qquad \text{which implies} \qquad Z = e^{-\beta E_1} + e^{-\beta E_2},$$

and so

$$P_1 = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2}}, \qquad P_2 = \frac{e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}}.$$

Once we have the probabilities of the different states, we can calculate statistical properties such as the mean energy of the system:

$$\langle E \rangle = E_1 P_1 + E_2 P_2 = \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}} = E_1 + \frac{E_2 - E_1}{1 + e^{\beta(E_2 - E_1)}}. \tag{6.3}$$

The mean energy $\langle E \rangle$, for a single particle, is never the energy of the system: the latter, at any given moment, is either E_1 or E_2. However, if we make many measurements of this energy, the average of these values will give a quantity which tends towards $\langle E \rangle$.

6.2.2 System consisting of N two-level particles

Let us now consider a system consisting of N two-level particles which do not interact with each other. We can check that the number of configurations of the system is 2^N; for example, for $N = 3$, the $2^3 = 8$ states are: $\{1, 1, 1\}$, $\{1, 1, 2\}$, $\{1, 2, 1\}$, $\{1, 2, 2\}$, $\{2, 1, 1\}$, $\{2, 1, 2\}$, $\{2, 2, 1\}$ and $\{2, 2, 2\}$, where the notation $\{x, y, z\}$ means that the first particle is in state x, the second in state y, and the third in state z.

Thanks to the independence of the particles, the Boltzmann formula is not required to calculate the mean energy of this N-particle system. We just need to write:

$$\text{total energy} = (\text{energy } 1^{\text{st}} \text{ particle}) + (\text{energy } 2^{\text{nd}} \text{ particle}) + \cdots + (\text{energy } N^{\text{th}} \text{ particle})$$

The average of a sum is equal to the sum of the averages. The average of any term of the right-hand side is given by (6.3). We can deduce that the mean total energy is

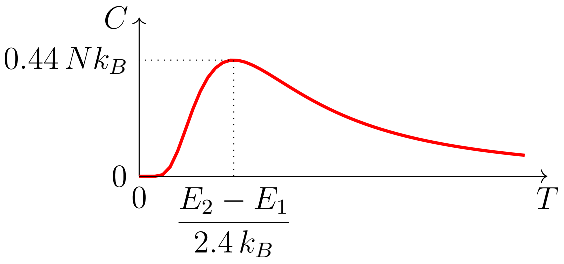
$$\langle \text{total energy} \rangle = N \langle \text{energy of a particle} \rangle = N \left(E_1 + \frac{E_2 - E_1}{1 + e^{\beta(E_2 - E_1)}} \right). \tag{6.4}$$

The expression (6.4) is an average, and the energy of the system at a given moment is never exactly equal to this value. However, if N is very large, the *law of large numbers* tells us that the difference between the energy of the system and its mean value is negligible. In thermodynamics, with $N \sim 10^{20}$, the difference between the energy of the system and its mean value is almost impossible to measure, and we identify (6.4) as the internal energy of the system:

$$U = N \left(E_1 + \frac{E_2 - E_1}{1 + e^{\beta(E_2 - E_1)}} \right). \tag{6.5}$$

This internal energy is an increasing function of the temperature (remember that $\beta = 1/(k_BT)$) and, by taking the derivative with respect to T, we obtain the thermal capacity C of the system. We invite you to make the calculation and to check that:

$$C = Nk_B\frac{X^2e^X}{(1+e^X)^2} \text{ with } X = \frac{E_2 - E_1}{k_BT}. \tag{6.6}$$



- In statistical mechanics, we can consider "small" systems (with a single particle, or just a few). We can then calculate probabilities and mean values, as in (6.3).
- For thermodynamics, the system considered must be "large" (with 10^{20} particles). We can then calculate the internal energy or the thermal capacity, as in (6.6).

Calculating thermodynamic quantities (internal energy, entropy, thermal capacity, *etc.*) for a "small" system would be meaningless.

6.2.3 High and low temperature limits, frozen states

The same system as in the previous section is still considered. We decide, to be specific, that $E_2 > E_1$ (state 1 is thus the *fundamental*, and state 2 the *excited* state). We can easily check with (6.5) that

- If $k_BT \gg E_2 - E_1$, then $\beta(E_2 - E_1) \ll 1$ and $U \approx N\frac{E_1+E_2}{2}$.
- If $k_BT \ll E_2 - E_1$, then $\beta(E_2 - E_1) \gg 1$ and $U \approx NE_1$.

The case $k_BT \gg E_2 - E_1$ is called the *high temperature limit*. The energy of the system is $U \approx N(E_1 + E_2)/2$ because there are as many particles in the fundamental (state 1, of energy E_1) as in the excited state (state 2, of energy E_2): the temperature is so high that the energy difference does not matter and all the microstates are equiprobable. Indeed, according to (6.2), we have $P_1/P_2 = e^{\beta(E_2-E_1)} \approx 1$: state 1 has almost the same probability as state 2.

The case $k_BT \ll E_2 - E_1$ is called the *low temperature limit*. The energy of the system is $U \approx NE_1$ because almost all the particles are in the fundamental. Indeed, according to (6.2), we have $P_1/P_2 = e^{\beta(E_2-E_1)} \gg 1$: state 1 is much more likely than state 2. In the low temperature limit, it is sometimes said that the system is "frozen": all the particles are "stuck" in the fundamental, and very few of them are excited.

Video 4

As explained in a video, the notions we have just introduced can be generalised to any quantum system. We will say that any system is in its *low temperature limit*, or that it is frozen, if k_BT is very small with respect to the *gap*, *i.e.* the difference of energy between the fundamental and the first excited state.

! The notions of "low temperature" and "high temperature" depend on the system under consideration. For example :

- In a simple atomistic model, the electronic cloud is (typically) in its low temperature limit if $T \ll 10^5\,\mathrm{K}$, *i.e.* always.
- The magnetisation of a paramagnetic metal is (typically) in its low temperature limit if $T \ll 1\,\mathrm{K}$, even for a very strong field, *i.e.* never.

These notions also depend on which property of the system we are looking at. For example, for a diatomic gas, in addition to moving around, a particle can rotate and vibrate. We find that

- Rotational properties are (typically) in the low temperature limit if $T \ll 100\,\mathrm{K}$, *i.e.* almost never.
- Vibration-related properties are (typically) in the low temperature limit if $T \ll 2\,000\,\mathrm{K}$, *i.e.* always in the usual conditions.

6.2.4 Energy fluctuations

For any thermodynamic system in contact with a thermostat, it is known that the energy of the system fluctuates but always remains close to its average value, the internal energy. We want to quantify the difference between the fluctuating energy and its average value.

Since the energy of the system is a random quantity (which depends on the microscopic configuration), we can calculate the probability for each energy. Let us write:

$$P(E) = (\text{probability that the system has energy } E).$$

To have the energy E, the system must be in a microstate σ such that $E(\sigma) = E$. The probability of *one* of these microstates is $P_\sigma = \frac{1}{Z}e^{-\beta E_\sigma} = \frac{1}{Z}e^{-\beta E}$, but we must not forget that there are *a priori* several microstates with the same energy E. We can write:

$$\Omega(E) = (\text{number of microstates } \sigma \text{ such that } E_\sigma = E).$$

(This is the same notation as in the previous chapter.) We then have

$$P(E) = \Omega(E)\frac{1}{Z}e^{-\beta E}.$$

! The following two quantities must not be confused with each other:

$$P_\sigma = \text{probability of being in a given microstate } \sigma,$$
$$P(E) = \text{probability of being in any microstate of energy } E.$$

Let us take the logarithm of $P(E)$:

$$\ln P(E) = -\beta\big[E - TS(E)\big] - \ln Z, \tag{6.7}$$

where we used Boltzmann's postulate $\ln \Omega(E) = \frac{1}{k_B}S(E) = \beta T S(E)$. We can see that:

The most probable energy is that which minimises $E - TS(E)$. (6.8)

Recall that T is the (fixed) temperature of the thermostat (we could have written it as T_0), and that E and $S(E)$ are the energy and entropy of the system, respectively. The quantity

$E - TS(E)$ is thus connected to the thermodynamic potential Φ for a system in contact with a thermostat, see frame 4.1. We have seen in thermodynamics that Φ must be minimal at equilibrium, which is consistent with (6.8).

We can call E^* the energy that minimises (6.7). Using an expansion around E^*, the first order being zero (since E^* is a minimum) , we obtain

$$\ln P(E) \approx -\beta\big[E^* - TS(E^*)\big] - \ln Z - \frac{(E-E^*)^2}{2k_B T^2 C_V} + \cdots \tag{6.9}$$

(Try to do this as a practice exercise. Do not forget that the temperature $T = T_0$ of the thermostat is constant.)

Taking the exponential of this relation, and considering E as a continuous variable, we obtain:

Frame 6.2 : **Energy fluctuations**

- For a thermodynamic system in contact with a thermostat, E has a Gaussian distribution:
$$P(E) \text{ is proportional to } \exp\left[-\frac{(E-E^*)^2}{2k_B T^2 C_V}\right].$$
- The most probable energy E^* is therefore equal to the mean energy $\langle E \rangle$, *i.e.* to the internal energy U.
- Energy fluctuations are characterised by the standard deviation σ:
$$|E - E^*| \text{ is of the order of } \sigma = \sqrt{k_B T^2 C_V}.$$

Remark: as C_V and $U = E^* = \langle E \rangle$ are extensive, they are proportional to the size N of the system. The standard deviation σ is proportional to $\sqrt{N}$, and σ/U is proportional to $1/\sqrt{N}$. When N is large (thermodynamic limit), this ratio tends to 0: the fluctuations are negligible.

6.2.5 Classical systems and continuous variables

Consider a classical system, for example a particle. To describe the system, we must give the position and velocity of the particle:

$$\sigma = \{\vec{r}, \vec{v}\} = \{x, y, z, v_x, v_y, v_z\}.$$

The energy of the particle is then a function of these six variables:

$$E_\sigma = E(x, y, z, v_x, v_y, v_z). \tag{6.10}$$

The difficulty here is that the variables used to describe the particle vary continuously. We must then abandon the idea of giving the individual probability of each microstate, and reason in terms of *probability density*. For a single variable q, we define the density $f(q)$ as follows: whatever $a < b$, we have

$$\int_a^b f(q)\,\mathrm{d}q = \text{probability that the random variable } q \text{ is between } a \text{ and } b.$$

For an infinitesimal interval $[a, b]$, we obtain

$$f(q)\,\mathrm{d}q = \text{probability that the random variable } q \text{ is between the numbers } q \text{ and } q + \mathrm{d}q.$$

The normalisation of this probability and its mean value are then written

$$\int f(q)\,\mathrm{d}q = 1, \qquad \langle q \rangle = \int q f(q)\,\mathrm{d}q.$$

Here, these two integrals are taken over the domain where the random variable q can vary. For example, depending on the case, these integrals can be $\int_{-\infty}^{\infty}$ if q is a velocity, or $\int_0^L$ if q is a coordinate in a box, or $\int_0^{2\pi}$ if q is an angle.

In the problem that interests us, there are six variables. We introduce a density function $f_\sigma = f(x, y, z, v_x, v_y, v_z)$ such that

$$\begin{aligned} &f(x, y, z, v_x, v_y, v_z)\,\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z\,\mathrm{d}v_x\,\mathrm{d}v_y\,\mathrm{d}v_z \\ &\qquad = \text{probability that} \begin{cases} \text{the position is } (x, y, z) \text{ to within } (\mathrm{d}x, \mathrm{d}y, \mathrm{d}z) \\ \qquad \text{and} \\ \text{the velocity is } (v_x, v_y, v_z) \text{ to within } (\mathrm{d}v_x, \mathrm{d}v_y, \mathrm{d}v_z) \end{cases} \end{aligned}$$

Not surprisingly, the basic result of frame 6.1 adapts directly to classical systems with continuous variables:

Video 5

Frame 6.3 : Boltzmann's factor for continuous variables

For a classical system in thermodynamic equilibrium and in contact with a thermostat at temperature T,

$$f_\sigma \ \text{ is proportional to } \exp\left(-\frac{E_\sigma}{k_B T}\right). \tag{6.11}$$

Let us take an example. In a cubic box, the sides of which have a length L, we consider a non-relativistic classical particle of mass m subjected to gravity. Its energy is

$$E_\sigma = E(x, y, z, v_x, v_y, v_z) = mgz + \frac{1}{2} m \vec{v}^2, \tag{6.12}$$

where x, y and z are in the interval $[0, L]$.

We apply (6.11), with $\beta = 1/(k_B T)$ and using "$\propto$" for "is proportional to":

$$f_\sigma = f(x, y, z, v_x, v_y, v_z) \propto e^{-\beta mgz}\, e^{-\beta \frac{1}{2} m \vec{v}^2}$$

We note that the position and velocity variables can be factorised:

$$f_\sigma = f_{\text{pos}}(x, y, z) f_{\text{vel}}(v_x, v_y, v_z) \text{ with } f_{\text{pos}} \propto e^{-\beta mgz} \text{ and } f_{\text{vel}} \propto e^{-\beta \frac{1}{2} m \vec{v}^2}$$

From a probability point of view, this means that *the position and velocity of the particle are independent random variables*: we can first determine the position from the density f_{pos} then, *independently of this position*, determine the velocity from the density f_{vel}.

The density f_{vel} is discussed in detail in the next section. Here, let us look at the density f_{pos}.

What we notice first is that f_{pos} depends only on z. This means that the variables x and y are chosen *uniformly* in the interval $[0, L]$: no value is favoured. On the other hand, the probability density f_{pos} decreases with the altitude z: *a priori*, the particles are more likely to be at the bottom rather than at the top. Let us see to what extent:

- For a molecule of dinitrogen (molar mass 28 g/mol) at room temperature, we find $\beta mg = 1/(8.700\,\mathrm{m})$. Unless the box is several kilometres high, we find that $\beta mgz \ll 1$ and $e^{-\beta mgz} \approx 1$ for all values of z. Thus we find that f_{pos} is, with a very good approximation, also independent of z; all the values of z are equiprobable and we conclude that we can neglect gravity to study a gas in a box.
- For a small grain of fine sand with a mass $m = 1\,\mu\mathrm{g}$ at room temperature, we find $\beta mg = 1/(4\,10^{-13}\,\mathrm{m})$. We see that $f_{\mathrm{pos}} \propto e^{-\beta mgz}$ is almost zero except for $z = 0$; the sand grains, even very light, remain at the bottom of the box; thermal agitation is not sufficient to lift them.

6.2.6 Kinetic theory of gases

We are now interested in the velocity distribution of a particle at thermodynamic equilibrium. The important result is the following:

Frame 6.4 : **Maxwell-Boltzmann distribution**

At thermodynamic equilibrium, particle velocities in a **classical** system are described by the Maxwell-Boltzmann distribution:

$$f_{\mathrm{vel}}(\vec{v}) \propto \exp\left[-\frac{m\vec{v}^2}{2k_BT}\right].$$

This implies that the mean translational kinetic energy of the particle is

$$\left\langle \frac{1}{2} m\vec{v}^2 \right\rangle = \frac{3}{2} k_B T. \tag{6.13}$$

Video 6

This result is explained in detail in a video.

In the previous section, we obtained the f_{vel} distribution for the case of a single particle in a box; this distribution remains valid for a **classical** system consisting of any number of particles, whatever the interaction potential or the external potential to which these particles are subjected to. In particular, it applies to the mouvement of atoms in solids, liquids or gases. However, it does not apply to the movement of electrons in a conductive metal, because these electrons have a strongly quantum behaviour.

6.2.7 Equipartition of energy

We started from a system consisting of one particle with an energy

$$E_\sigma = \frac{1}{2} m\vec{v}^2 + V(x, y, z),$$

with V the external potential acting on the particle. At thermodynamic equilibrium, the mean energy of the particle is

$$\langle E \rangle = \left\langle \frac{1}{2} m\vec{v}^2 \right\rangle + \big\langle V(x, y, z) \big\rangle = \frac{3}{2} k_B T + \big\langle V(x, y, z) \big\rangle,$$

where we used (6.13) for the mean kinetic energy. (Exercise: would you know how to calculate $\big\langle V(x,y,z)\big\rangle$ in the simple case where $V = mgz$ for a particle in a box?)

It is remarkable that the mean kinetic energy is independent of the particle mass m. In fact, if we assume that the energy of the system is written in the form

$$E_\sigma = \cdots + bq^2 + \cdots ,$$

where q is one of the variables used to describe the system (q can be a position, a velocity, an angle, a kinetic moment, ...), then we can verify that the mean energy is written

$$\langle E\rangle = \langle\cdots\rangle + \frac{1}{2}k_BT + \langle\cdots\rangle.$$

This is the energy equipartition theorem.

Frame 6.5 : Energy equipartition theorem

Video 7

For a **classical** system at equilibrium in contact with a thermostat at temperature T, each *quadratic* term of the energy of the system has a mean value equal to $\frac{1}{2}k_BT$.

Remarks:

- $\frac{1}{2}m\vec{v}^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$. There are *three* kinetic energy quadratic terms, hence the result (6.13).
- For any classical system consisting of N particles, the mean translational kinetic energy is therefore $\langle E_{\text{trans}}\rangle = \frac{3}{2}Nk_BT$.
- For an ideal monoatomic gas, $U = \langle E_{\text{trans}}\rangle = \frac{3}{2}Nk_BT$.
- Similarly, we can find the internal energy of an ideal diatomic gas using the energy equipartition theorem; see the video.

6.3 Demonstration of (6.1)

Finally, we will now demonstrate (6.1). The aim is to calculate the equilibrium probability P_σ that a system in contact with a thermostat would be in the microstate σ.

Let us start with the thermostat alone. We denote by $\Omega_{\text{th}}(U)$ the number of microstates of the thermostat when its internal energy is U. According to Boltzmann's postulate, the entropy of the thermostat for this internal energy is

$$S_{\text{th}}(U) = k_B \ln \Omega_{\text{th}}(U). \tag{6.14}$$

The thermostat does not receive work; the thermodynamic identity is therefore written

$$\mathrm{d}U = T\,\mathrm{d}S_{\text{th}}.$$

But the temperature of a thermostat remains constant even when its internal energy changes. We can thus integrate the relation:

$$\Delta U = T\,\Delta S_{\text{th}} \qquad \textit{i.e.} \qquad S_{\text{th}}(U) = \frac{U}{T} + \text{Cst}.$$

Combining with (6.14), we get

$$\Omega_{\text{th}}(U) = \exp\left[\frac{U}{k_B T} + \frac{\text{Cst}}{k_B}\right] \propto \exp\left[\frac{U}{k_B T}\right]. \tag{6.15}$$

We now assume that the system we want to study is in contact with the thermostat. The $\{\text{system} + \text{thermostat}\}$ entity is isolated, we note E_{tot} the (constant!) energy of this entity and Ω_{tot} its total number of microstates. According to Boltzmann's postulate, **all the microstates in the {system + thermostat} entity are equiprobable**, and their probability is $1/\Omega_{\text{tot}}$.

Let us select a microstate σ of the system alone (without the thermostat), *i.e.* let us choose the positions and velocities for all the particles in the system. For this microstate, the energy of the system is E_σ (a function of the velocities and positions) and, consequently, the thermostat has an energy $E_{\text{tot}} - E_\sigma$. The thermostat can therefore be in any of the $\Omega_{\text{th}}(E_{\text{tot}} - E_\sigma)$ microstates corresponding to this energy.

So we see that among the Ω_{tot} microstates of the $\{\text{system} + \text{thermostat}\}$ entity, there are $\Omega_{\text{th}}(E_{\text{tot}} - E_\sigma)$ such that the system is in state σ. The probability P_σ is then written as (number of favorable cases) / (total number of cases), *i.e.*

$$P_\sigma = \frac{\Omega_{\text{th}}(E_{\text{tot}} - E_\sigma)}{\Omega_{\text{tot}}}.$$

Then we just need to use (6.15) to get the desired result.

Chapter 7

Video 1

Phase changes of a pure substance

By definition, a pure substance contains only one kind of molecule (H_2O, Fe, C, ethanol, *etc*). It can be in a solid, liquid or gaseous phase.

However, nature is richer than just these three forms. A pure substance can have different solid phases corresponding to different crystalline orders (at the microscopic level the atoms are arranged in space in different ways according to their phases). Water, for example, in addition to regular ice, has more than ten types of high-pressure ice phases. Another well known example is carbon: depending on temperature and pressure, carbon can be in the diamond or graphite phase!

In addition, a substance is not limited to its solid, liquid and gas phases:

- Depending on the temperature or the magnetic field applied, a material may have permanent magnetisation (it can be a magnet). In the absence of a magnetic field, we will then talk of *ferromagnetic* phase when the material has a non-zero magnetisation, and of a *paramagnetic* phase when it has no magnetisation. The field of magnetism also contains many other phases the presentation of which exceeds the objectives of this course.
- When their temperature is lowered, some substances (*e.g.* mercury, lead, aluminium) see their electrical resistance tend to zero. The material is a *superconductor* (*superconducting* phase). A superconducting electrical wire with a current flowing through it does not heat up, which means there is no Joule effect! This happens below a certain temperature, the critical temperature, which is usually very close to 0 K. It is 4 K for mercury, 7 K for lead and 1 K for aluminium. In physics, the experimental and theoretical study of superconducting materials is a very dynamic area of research.
- The *superfluid* phase was observed for the first time in liquid helium-4 at very low temperature (approximately 2 K). In this phase, helium flows without viscosity!
- To finish this introduction, we can also mention other phases such as liquid crystals, ferroelectrics, plasmas, *etc.*

7.1 Equilibrium condition and evolution towards equilibrium

Consider a pure substance at temperature T and pressure p (imposed by a reservoir) composed of two phases α and β. The thermodynamic potential best adapted is therefore the

Gibbs free energy G. n_α and n_β are the numbers of moles in phases α and β, respectively, and μ_α and μ_β their chemical potentials. The thermodynamic identity at a given T and p is $\mathrm{d}G = \mu_\alpha\,\mathrm{d}n_\alpha + \mu_\beta\,\mathrm{d}n_\beta$. However, since the total amount of substance $n_\alpha + n_\beta$ remains constant (for the closed system we are considering), we have $\mathrm{d}n_\alpha = -\mathrm{d}n_\beta$ and

$$\mathrm{d}G = [\mu_\alpha(T,p) - \mu_\beta(T,p)]\,\mathrm{d}n_\alpha. \tag{7.1}$$

However, we have seen that at equilibrium, G must be minimum. Three cases arise:

- If $\mu_\alpha(T,p) > \mu_\beta(T,p)$. Then, necessarily $\mathrm{d}n_\alpha < 0$: the substance goes from phase α to phase β until $n_\alpha = 0$. At equilibrium, only phase β is present.
- If $\mu_\beta(T,p) > \mu_\alpha(T,p)$. By the same reasoning, phase β diminishes until only phase α is left at equilibrium.
- If $\mu_\beta(T,p) = \mu_\alpha(T,p)$. Then $\mathrm{d}G = 0$, whatever the value of n_α.

We therefore come to the following conclusions:

Frame 7.1 : Condition for the coexistence of two phases

- When there is coexistence between two phases at thermodynamic equilibrium, their chemical potentials are equal:

$$\mu_\alpha(T,p) = \mu_\beta(T,p). \tag{7.2}$$

  The Gibbs free energy G is then independent of the distribution of the substance between the two phases.
- Conversely, when the chemical potentials of two phases are equal, there is the possibility of coexistence between these two phases.

At a given temperature T, the coexistence pressure can be defined:

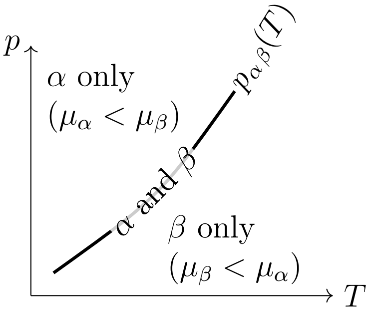
$$p_{\alpha\,\beta}(T) = (\text{pressure at which the two phases } \alpha \text{ and } \beta \text{ coexist}). \tag{7.3}$$

This pressure is obtained by solving $\mu_\alpha(T, p_{\alpha\,\beta}(T)) = \mu_\beta(T, p_{\alpha\,\beta}(T))$. In the case of liquid-vapour equilibrium, it is called the "equilibrium vapour pressure" and is noted

$$p_{\mathrm{S}}(T) = p_{\mathrm{L\,G}}(T) = (\text{equilibrium vapour pressure}).$$

7.2 Phase diagram

Video 2

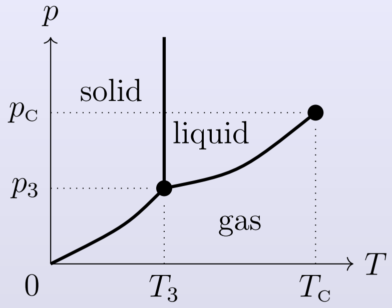


In the (T, p) diagram, see adjacent figure, the coexistence pressure $p_{\alpha\,\beta}(T)$ is a line that separates the region consisting only of phase α and where $\mu_\alpha(T, p) < \mu_\beta(T, p)$, from the region consisting only of phase β and where $\mu_\alpha(T, p) > \mu_\beta(T, p)$.

By generalising this scheme to take into account the three phases of a (pure) substance, we obtain the phase diagram.

Frame 7.2 : **Phase diagram of a pure substance**

Experimentally, for a pure substance, there are three possible phases: solid, liquid and gas, and a phase diagram typically looks like this:



- The *triple point* (T_3, p_3) is the meeting point of the three coexistence lines between two phases (liquid-gas, liquid-solid and solid-liquid). It is the only point where the three phases can coexist. The coordinates of the triple point are obtained as the (unique) solution of the equations $\mu_{\text{solid}}(T_3, p_3) = \mu_{\text{liquid}}(T_3, p_3)$ and $\mu_{\text{solid}}(T_3, p_3) = \mu_{\text{gas}}(T_3, p_3)$. (Two equations for two unknowns.)
- Another remarkable point is the *critical point* (T_C, p_C) where the liquid-gas coexistence line stops: to the right of the critical point, there is only one phase. This is called a *supercritical* fluid (or gas).
- For example, for water, $T_3 = 0.01°\text{C}$, $p_3 = 611.2\,\text{Pa}$, $T_C = 374.15°\text{C}$ and $p_C = 22.12\,\text{MPa}$. For oxygen, $T_3 = -218.8°\text{C}$, $p_3 = 146\,\text{Pa}$, $T_C = -118.67°\text{C}$ and $p_C = 5.04\,\text{MPa}$. In particular, oxygen is supercritical at room temperature $(T > T_C)$ and cannot be liquified simply by increasing the pressure.

Video 3

To take a typical example, the phase diagram of carbon dioxide (CO_2) is shown in Figure 7.1.

In a phase diagram, the solid/gas and liquid/gas coexistence lines always have a positive slope. The solid/liquid line usually has a very important positive slope (the line is almost vertical, but leans slightly to the right). There is however a limited number of exceptions, for which the solid/liquid line has a negative slope (the line leans slightly to the left): water (H_2O) the diagram of which is represented in Figure 7.2, silicon (Si), gallium (Ga), bismuth (Bi), antimony (Sb), germanium (Ge) and plutonium (Pt).

Note, on the phase diagram of water, Figure 7.2, the large number of different solid phases at high pressures.

Finally, the phase diagram of helium-4 is represented in Figure 7.3 with its superfluid phase. You will notice that helium has the remarkable property of remaining liquid under

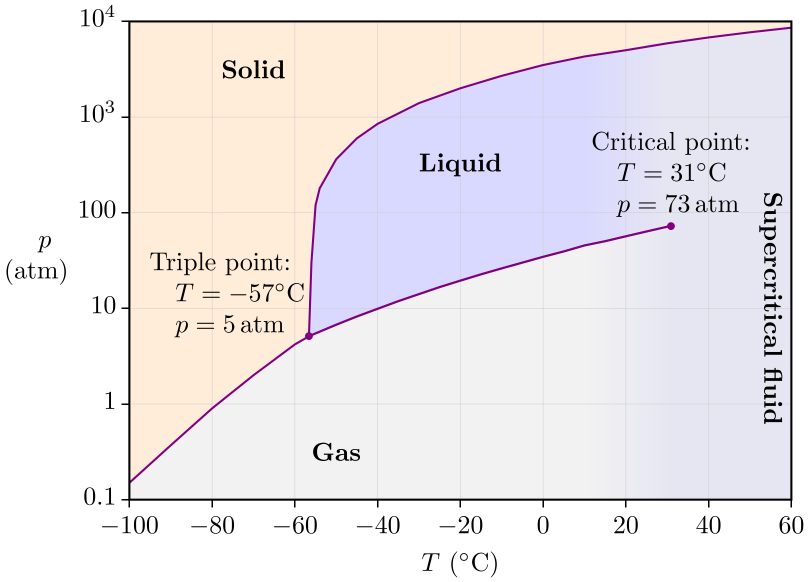


Figure 7.1: Phase diagram of CO_2. Note the logarithmic scale of the pressure which makes it possible to display on the same figure a very wide range of pressures.

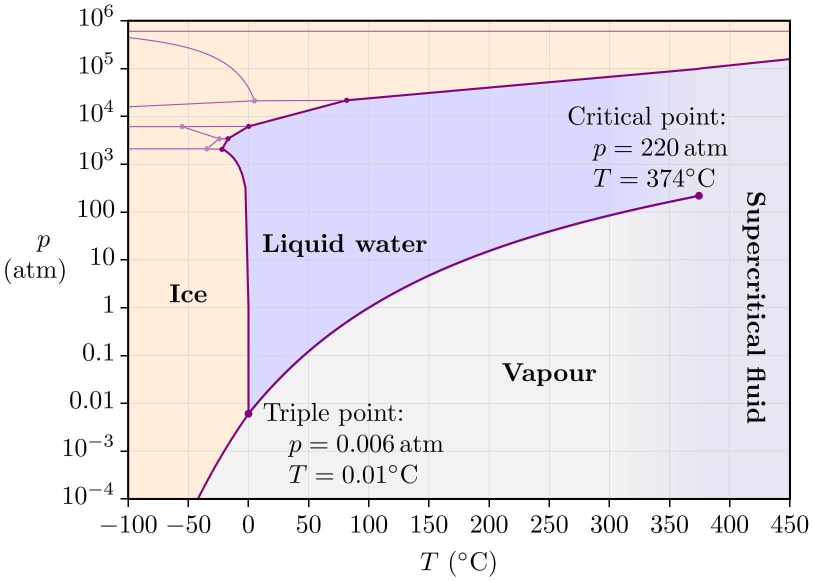


Figure 7.2: Phase diagram of water, with a logarithmic scale for the pressure. There are several different solid phases in the orange region.

a pressure of 1 atm, no matter how low the temperature is! A minimum pressure of 25 atm must be applied for helium to change to a solid phase.

7.3 Isothermal diagrams

At a given temperature T, we want to study the pressure as a function of volume. In order to consider only intensive quantities, the pressure p is plotted as a function of the molar volume $v = V/n$. (It is also possible to plot p as a function of the specific volume $v_m = V/m$.) Such

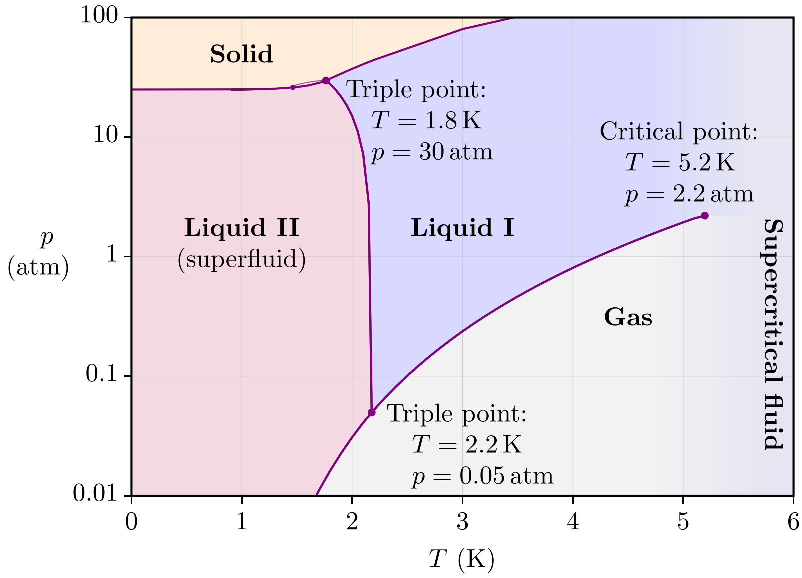


Figure 7.3: Phase diagram of helium-4, with a logarithmic scale for the pressure. At low temperatures, helium is in the *superfluid* phase.

a plot is called a *Clapeyron diagram.* Figure 7.4 shows isothermal curves for three different temperatures. Each of these curves would correspond to a vertical line (T = constant) in the (T, p) phase diagram of frame 7.2. We note the following points:

- At high temperature $T = T_1 > T_\mathrm{C}$, the substance behaves like an ideal gas: $p \approx RT/v$. The curve corresponds to the branch of an hyperbola.
- At the critical temperature $T = T_\mathrm{C}$, there is no plateau but the slope of the curve becomes null at pressure p_C. This is the critical point; the distinction between gas and liquid phases is about to be emerge.
- At low temperature $T = T_2 < T_\mathrm{C}$, the curve $p(v)$ has a *pressure plateau* (*i.e.* the pressure becomes independent of the molar volume v). The value of p on this plateau is $p_\mathrm{S}(T_2)$, the equilibrium vapour pressure at the considered temperature. At that point, the gas and liquid phases coexist. On the right hand-side of the plateau (when the volume is large) the system is in a gaseous phase whereas on the left (when the volume is small) it is in a liquid phase.

The curves in Figure 7.4 were obtained for a van der Waals gas, see frame 1.10. However, it is not directly possible to obtain an isotherm with a plateau from the van der Waals equation of state as seen for temperature T_2. The precise construction of this figure is explained in a video.

Video 4

Imagine a system that follows from right to left the isotherm $T_2 < T_\mathrm{C}$ of Figure 7.4. Initially (right) the system has a large molar volume v and is in gaseous form. The pressure increases slowly while the molar volume decreases. When the system reaches the right end of the plateau (at point M_G), the first liquid drop appears. From this point, and as long as the system follows the plateau, the pressure no longer changes when the volume is decreased; on the other hand, more and more gas is liquefied. At the left end of the plateau (at point M_L), the last gas bubble disappears. From this point, the pressure increases again when the volume is decreased. In fact, as the system is totally in the liquid phase and therefore not very compressible, the pressure increases very quickly with the volume (the slope is steep).

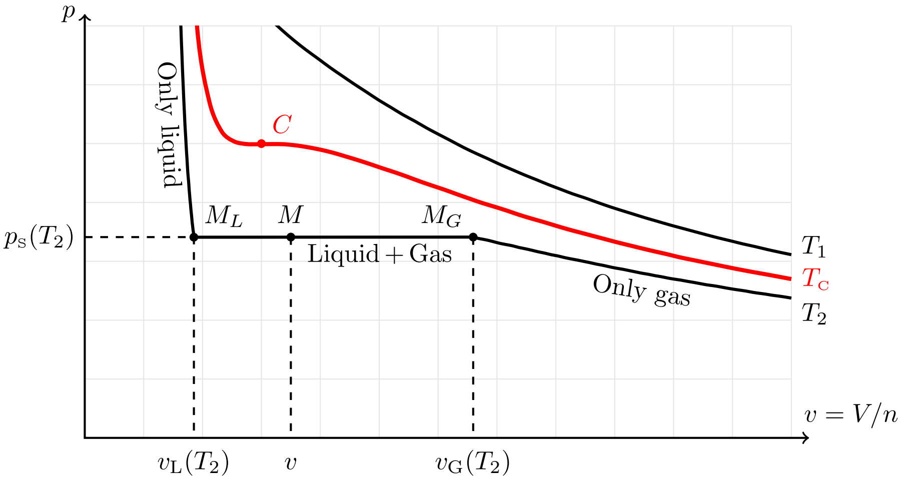


Figure 7.4: Three isotherms in a (p, v) diagram. The pressure plateau indicates the coexistence of the liquid (L) and gaseous (G) phases.

On the plateau, as the liquid and gaseous phases coexist, the pressure is given by the equilibrium vapour pressure $p_S(T_2)$ at the considered temperature T_2, see frame 7.1. Under these temperature and pressure conditions, the molar volumes of the gas and the liquid are v_G and v_L, respectively, the x-coordinates of points M_G and M_L.

Consider a system whose state is represented by a point M of this plateau. The aim is to determine the molar fraction of the gas x_G = (number of moles of gas)/(total number of moles). (The molar fraction of the liquid is of course $x_L = 1 - x_G$.) By taking n the amount of substance in the system, the volume occupied by the gas is $nx_G v_G$, and the volume occupied by the liquid is $n(1 - x_G)v_L$. The total volume is therefore written

$$V = nx_G v_G + n(1 - x_G)v_L = nv,$$

with v the x-coordinate of point M. We deduce that

$$x_G = \frac{v - v_L}{v_G - v_L} = \frac{(\text{distance between } M_L \text{ and } M)}{(\text{distance between } M_L \text{ and } M_G)}. \tag{7.4}$$

This is the *lever rule*, which allows to determine the fraction of vapour from diagram 7.4 using lengths $M_L M$ and $M_L M_G$. By varying the temperature, the different regions corresponding to the different states of the system can be drawn in the (p, v) diagram: liquid, gas, or coexistence of the liquid and gaseous phases; see Figure 7.5. (The isotherms of Figure 7.4 are also shown.) The lower the temperature, the wider the coexistence phase. The critical point (v_C, p_C) is located at the top of the bell-shaped curve, at temperature T_C. Above the critical isotherm, the differences between liquid and gas disappear and the fluid is said to be supercritical. The curve to the left of C is called the bubble-point curve, the curve to the right is the dew-point curve.

So far, this study only considered fluid phases, but by lowering the temperature, or increasing the pressure, the solid phase must appear. The regions corresponding to the different phases will then look like those shown in Figure 7.6. Can you find the triple point? (Hint: the triple point is not a simple point on the (p, v) diagram, but corresponds to a line.)

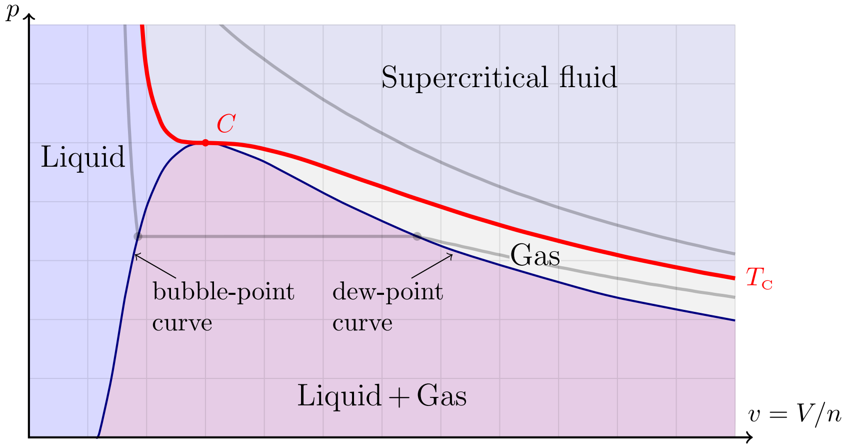


Figure 7.5: In the (p, v) diagram, regions corresponding to the different states of the system are indicated.

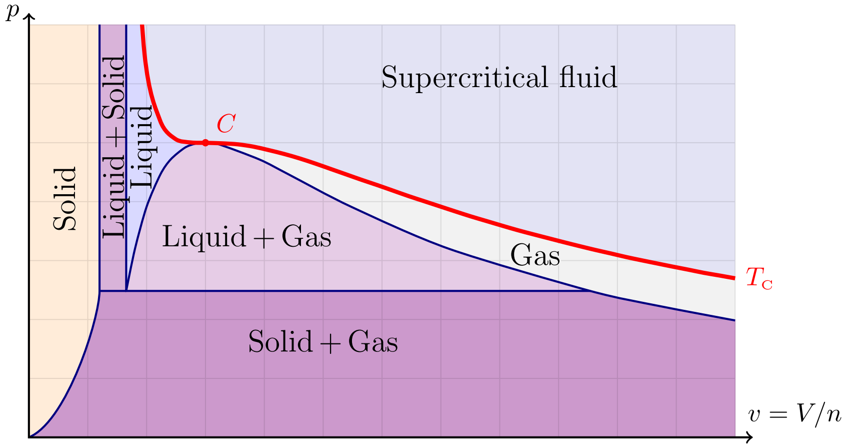


Figure 7.6: Coexistence regions of the solid, liquid and gas phases in a pressure-volume diagram.

7.4 Latent heat

The phase changes between a phase α and a phase β at fixed p *or* T, actually occur at fixed p *and* T. This is because, throughout the transition, phases α and β coexist and the pressure must be equal to the coexistence pressure: $p = p_{\alpha\beta}(T)$.

Consider, at fixed p and T, the reversible transformation of a state A where all the substance is in phase α into a state B with all the substance in phase β. We want to calculate the heat Q received by the system. The transformation is isobaric, so $Q = \Delta H$, see (4.28). But the transformation is also reversible and isothermal, so $Q = T\Delta S$, see (3.7). Thus we have $\Delta H = T\Delta S$ or, by labelling the molar quantities using lower-case letters (*i.e.* $h = H/n$ is the molar enthalpy, $s = S/n$ is the molar entropy, *etc.*),

$$\Delta h = T\Delta s$$

This enthalpy variation is called the molar latent heat.

Video 5

Frame 7.3 : Latent heat

The *latent heat* is defined as the heat required to change the system from one phase to another. We have:

- the latent heat of vaporisation or enthalpy of vaporisation (heat required to pass from liquid to gas),
- the latent heat of fusion or enthalpy of fusion (heat required to pass from solid to liquid),
- the latent heat of sublimation or enthalpy of sublimation (heat required to pass from solid to gas).

These three latent heats are positive. If we write $l_{\alpha\beta}$ the *molar* latent heat to pass from phase α to phase β, we have

$$l_{\alpha\beta} = h_\beta - h_\alpha = T\left(s_\beta - s_\alpha\right). \tag{7.5}$$

The molar latent heat $l_{\alpha\beta}$ at temperature T is related to the coexistence pressure $p_{\alpha\beta}(T)$ between these two phases by the *Clausius-Clapeyron formula*, demonstrated below:

$$l_{\alpha\beta} = T\left(v_\beta - v_\alpha\right)\frac{\mathrm{d}p_{\alpha\beta}}{\mathrm{d}T}, \tag{7.6}$$

where v_α and v_β are the molar volumes of phases α and β, respectively.

Remarks:

- $\Delta H = T\Delta S$ can also be written as (since T is constant) $\Delta G = 0$ and, since $G = \mu n$, we retrieve $\mu_\alpha = \mu_\beta$, see frame 7.1.
- For gas→liquid, gas→solid or liquid→solid transformations, the heat required must be negative and equal to the opposite of, respectively, the vaporisation, melting or sublimation enthalpy, respectively.
- An example of a numerical value is the latent heat of vaporisation of water at 1 bar. For the *molar* latent heat we have $l_{\text{vap}} = 40.7\,\text{kJ.mol}^{-1}$. Recalling that the molar mass of water is $M_{\text{water}} = 18$ g/mol, we get the *specific* latent heat of vaporisation $L_{\text{vap}} = l_{\text{vap}}/M_{\text{water}} = 2.26\,10^3\,\text{kJ.kg}^{-1}$. It is therefore necessary to provide several millions of Joules to evaporate one litre of water!
- A consequence of the Clausius-Clapeyron formula is that if $l_{\alpha\beta} > 0$, then $v_\beta - v_\alpha$ and $\frac{\mathrm{d}p_{\alpha\beta}}{\mathrm{d}T}$ have the same sign. For most pure substances, $v_{\text{solid}} < v_{\text{liquid}} < v_{\text{gas}}$ and since l_{fusion}, $l_{\text{vaporisation}}$ and $l_{\text{sublimation}}$ are positive, we deduce that the slopes of the coexistence lines of the phase diagram are positive, see frame 7.2. However, for water, $v_{\text{ice}} > v_{\text{liquid}}$ which implies that the solid-liquid coexistence line has a negative slope.
- $\frac{\mathrm{d}p_{\text{fusion}}}{\mathrm{d}T}$ can also be estimated for water close to 0°C using (7.6), the density of ice $M_{\text{ice}} = 0.92\,\text{g}\,\text{cm}^{-3}$ and the latent heat of fusion $L_{\text{fusion}} = 334\,\text{kJ.kg}^{-1}$. The result is $\frac{\mathrm{d}p_{\text{fusion}}}{\mathrm{d}T} \approx -1.4\,10^7\,\text{Pa.K}^{-1}$, which means that the pressure must be increased by 140 bar for the melting temperature to drop by 1°C. Will you be able to repeat this calculation?

To prove the Clausius-Clapeyron formula (7.6), we start from the equality between the chemical potentials of the two phases along the coexistence line $p = p_{\alpha\beta}(T)$:

$$\mu_\alpha\big(T, p_{\alpha\beta}(T)\big) = \mu_\beta\big(T, p_{\alpha\beta}(T)\big).$$

By differentiating this equation with respect to T:

$$\left.\frac{\partial \mu_\alpha}{\partial T}\right|_p + \left.\frac{\partial \mu_\alpha}{\partial p}\right|_T \times \frac{\mathrm{d}p_{\alpha\,\beta}}{\mathrm{d}T} = \left.\frac{\partial \mu_\beta}{\partial T}\right|_p + \left.\frac{\partial \mu_\beta}{\partial p}\right|_T \times \frac{\mathrm{d}p_{\alpha\,\beta}}{\mathrm{d}T},$$

and using the Gibbs-Duhem relation (4.19) which gives the partial derivatives of the chemical potential with respect to the pressure and the temperature: $(\partial\mu/\partial T)_p = -s$ and $(\partial\mu/\partial p)_T = v$, we find $-s_\alpha + v_\alpha \frac{\mathrm{d}p_{\alpha\,\beta}}{\mathrm{d}T} = -s_\beta + v_\beta \frac{\mathrm{d}p_{\alpha\,\beta}}{\mathrm{d}T}$, or

$$s_\beta - s_\alpha = (v_\beta - v_\alpha)\,\frac{\mathrm{d}p_{\alpha\,\beta}}{\mathrm{d}T}.$$

Using (7.5), we obtain the Clausius-Clapeyron formula (7.6).

As explained in a video, on can try, from the Clausius-Clapeyron formula and under some hypotheses, to compute the liquid/gas coexistence line $p_{\mathrm{s}}(T)$.

Video 6

Chapter 8

Video 1

Binary solutions

In this chapter, we consider mixtures of *two* constituents, first as a single phase, then in different phases. Typical examples are water (H_2O) and salt (NaCl) (*brine*), water and sugar, water and alcohol (ethanol) in liquid phases, but also in both the liquid and gaseous phases.

8.1 Gibbs' phase rule

Let a mixture have c constituents indexed by the letter $i \in \{1, \ldots, c\}$. (In the following, we will consider binary solutions and c will be equal to two.) We ask the following question: what are the conditions for the system to be at thermodynamic equilibrium under ϕ phases? The phases are indexed by α or $\beta \in \{1, \ldots, \phi\}$, and we note:

$$\begin{aligned} n_i^\alpha &= (\text{number of moles of constituent } i \text{ in phase } \alpha), \\ n^\alpha &= \sum_i n_i^\alpha = (\text{total number of moles in phase } \alpha), \\ x_i^\alpha &= \frac{n_i^\alpha}{n^\alpha} = (\text{the \textit{molar fraction} of constituent } i \text{ in phase } \alpha). \end{aligned} \tag{8.1}$$

The molar fraction x_i^α verifies

$$0 \leq x_i^\alpha \leq 1, \qquad \sum_i x_i^\alpha = 1. \tag{8.2}$$

Extensive parameters are taken as the ϕ values n^α; the intensive parameters of the problem are therefore p, T and all the x_i^α. Taking into account condition (8.2), for each phase α, there are $c - 1$ independent values of x_i^α. The number of intensive parameters is therefore equal to $2 + \phi\,(c - 1)$.

In addition, to be in thermodynamic equilibrium, for *each species* i, the chemical potentials in the different phases must be equal: $\mu_i^\alpha = \mu_i^\beta$. This gives $\phi - 1$ equalities for each of the constituents, *i.e.* $c(\phi - 1)$ equations in total. We deduce that the number v of independent intensive variables, called *variance*, is $v = 2 + \phi\,(c - 1) - c\,(\phi - 1)$, hence

Frame 8.1 : **Gibbs' phase rule**

The variance v of a thermodynamic system composed of c constituents under ϕ phases is the number of independent intensive parameters. It is given by

$$v = 2 + c - \phi. \tag{8.3}$$

Examples:

- *Case of a pure substance* : $c = 1$ and we have $v = 3 - \phi$.
    - If $\phi = 1$ (the system is in a single phase), then we have $v = 2$ intensive variables: the pressure p and the temperature T.
    - If $\phi = 2$ (the system is in equilibrium between two phases), then there is only $v = 1$ independent intensive variable, for example T. For each given T, there is only one possible pressure for which two phases are in equilibrium; it is the coexistence pressure of the two phases, see frame 7.1.
    - If $\phi = 3$, then $v = 0$. The pressure and the temperature are fixed; it is the triple point.
- *Case of a binary solution* : $c = 2$ and we have $v = 4 - \phi$.
    - If $\phi = 1$, then $v = 3$. We can independently choose the values p, T and x_1 (or $x_2 = 1 - x_1$). At a given T, the state of the system can be represented in a diagram p versus x_1.
    - If $\phi = 2$, then $v = 2$. The two independent intensive variables are, for example, the temperature T and x_1^α (molar fraction of species 1 in phase α); the pressure p and x_1^β (molar fraction in the other phase $\beta \neq \alpha$) are fixed. Another possible choice is to impose the values of T and p; in this case, the molar fractions $x_1^\alpha(p, T)$ and $x_1^\beta(p, T)$ in phases α and β are fixed. We will come back in detail on this case.
    - If $\phi = 3$, then $v = 1$. For each given T, there is only one possible value of the pressure and of the three fractions x_1^α, x_1^β and x_1^γ of species 1 in the corresponding phases α, β and γ. In a (p, T) diagram, we have a triple line.
    - If $\phi = 4$, then $v = 0$. There is only one possible value for p, T and $\{x_1^\alpha\}$.

8.2 Single phase binary solutions

In this section, $\phi = 1$ and $c = 2$. The variance is $v = 3$.

8.2.1 Mixture of two ideal gases, ideal mixture

Imagine a homogeneous system in a volume V at temperature T, consisting of two species 1 and 2 in the gas phase (numbers of moles n_1 and n_2). The gases are considered as ideal, *i.e.* the interactions between particles of type 1, between particles of type 2 and between particles of type 1 and 2 are neglected. It is an *ideal mixture of ideal gases.*

The internal energy of the whole system is the sum of the internal energies that each of the gases would have if they were alone in the volume V at temperature T. This is also the case for entropy, and therefore for the free energy:

$$\begin{aligned} U(T,V,n_1,n_2) &= U_1(T,V,n_1) + U_2(T,V,n_2), \\ S(T,V,n_1,n_2) &= S_1(T,V,n_1) + S_2(T,V,n_2), \\ F(T,V,n_1,n_2) &= F_1(T,V,n_1) + F_2(T,V,n_2). \end{aligned} \tag{8.4}$$

(Remarks: U, U_1 and U_2 do not depend on V! U, S and F are additive because the two ideal gases do not interact: everything occurs as if the particles of species 1 and 2 were in different volumes.)

Deriving (8.4) with respect to V, the thermodynamic identity adapted to F gives

$$p = -\left.\frac{\partial F}{\partial V}\right|_{T,n_1,n_2} = -\left.\frac{\partial F_1}{\partial V}\right|_{T,n_1} - \left.\frac{\partial F_2}{\partial V}\right|_{T,n_2}.$$

$p_1 = -\left.\frac{\partial F_1}{\partial V}\right|_{T,n_1}$ is the pressure that n_1 moles of species 1 would have in volume V at temperature T. It is called the *partial pressure of species* 1.

Frame 8.2 : Partial Pressures

In a gas mixture, the *partial pressure of gas i* is referred to as the pressure p_i that the system would have if gas i were alone in the same volume at the same temperature.

For a mixture of two *ideal* gases, we have *Dalton's laws*:

$$p = p_1 + p_2 \qquad \text{(for an ideal gas).}$$

By writing $pV = nRT = (n_1 + n_2)RT$ and $p_iV = n_iRT$, we obtain easily

$$p_i = \frac{n_i}{n_1 + n_2} p = x_i\, p \qquad \text{(for an ideal gas),} \tag{8.5}$$

where we recall that x_i is the molar fraction of species i.

Remark: these results are easily generalised to a mixture of any number of ideal gases.

We now derive (8.4) with respect to n_1; the thermodynamic identity gives the chemical potential of species 1 in the mixture

$$\mu_1 = \left.\frac{\partial F}{\partial n_1}\right|_{V,T,n_2} = \left.\frac{\partial F_1}{\partial n_1}\right|_{V,T} \tag{8.6}$$

We recognize in the term on the right-hand side the chemical potential that species 1 would have if its n_1 moles of gas were alone in volume V at temperature T, the pressure, being by definition, equal to the partial pressure $p_1 = x_1\, p$. Hence, we can write

$$\mu_1(T,p,x_1) = \mu_1^0(T,p_1) = \mu_1^0(T,x_1 p), \tag{8.7}$$

with μ_1^0 the chemical potential of an ideal gas consisting of species 1 alone.

To go further, we need to know more about the chemical potential μ^0 of an ideal gas consisting of a single species. For an ideal gas, the Gibbs-Duhem relation (4.19) gives $\partial\mu^0/\partial p\big|_T = V/n = RT/p$. By integrating with respect to p at fixed T, we find

$$\mu^0(T,p) = RT\ln(p) + f(T), \qquad \text{(for an ideal gas)} \tag{8.8}$$

where the integration constant $f(T)$ is of course independent of p, but depends on T and the nature of the gas. From this expression, we can obtain $\mu^0(T, x_1 p) = \mu^0(T, p) + RT\ln(x_1)$ and, finally:

Video 2

Frame 8.3 : Ideal mixture

- For an ideal mixture of several **ideal gases**, the chemical potential of species i is given by
$$\mu_i(T, p, x_i) = \mu_i^0(T, p) + RT\ln(x_i), \tag{8.9}$$
where μ_i^0 is the chemical potential of species i alone (pure) and x_i its molar fraction.
- For a mixture of **any number of substances**, we say that we have an *ideal mixture* if the chemical potential of each species satisfies an equation of the form of (8.9). This is the Lewis-Randall rule.

Remarks:

- For an ideal mixture of liquids, $\mu_i^0(T, p)$ in (8.9) is of course the chemical potential of the liquid n° i, and not the chemical potential of an ideal gas.
- In a mixture of real gases, if the interactions are negligible, one will often be able to consider that the mixture is ideal (limit of the ideal gases). More surprisingly, many mixtures of liquids such that the molecules have similar sizes and structures are well described by the ideal mixture equation.
- Exercise: from (8.9), show that if we mix (at fixed p and T) a volume V_1 of pure species 1 and a volume V_2 of pure species 2 and that the mixture is ideal, then the total volume is $V_1 + V_2$.
- If $1\,\ell$ of water is mixed with $1\,\ell$ of ethanol, the mixture is $1.92\,\ell$. This mixture is not ideal.

8.2.2 Dilute solutions

In a binary mixture under a single phase, one of the two compounds is now considered in the minority; for example $n_2 \ll n_1$, and thus $x_1 \simeq 1$ and $x_2 \ll 1$. In this case, species 1 is the *solvent* and species 2 the *solute*. A very general calculation (detailed at the end of this section) gives for this diluted limit:

Frame 8.4 : Dilute solutions

In a dilute solution, the chemical potential of the solvent is

$$\mu_1(T, p, x_2) \approx \mu_1^0(T, p) - RTx_2 \qquad \text{when } x_2 \to 0, \tag{8.10}$$

where the function $\mu_1^0(T, p)$ is the chemical potential of the pure solvent.
The chemical potential of the solute verifies

$$\mu_2(T, p, x_2) \approx \Psi(T, p) + RT\ln(x_2) \qquad \text{when } x_2 \to 0, \tag{8.11}$$

where the function $\Psi(T, p)$ is not specified.

Note that, formally, we could have obtained (8.10) by writing $RT\ln(x_1) = RT\ln(1-x_2) \approx$

$-RTx_2$ in (8.9). However, the result of this section is not restricted to gaseous phases or ideal mixtures. For example, it is often applied to liquid phases.

Application: osmotic pressure

Video 3

The phenomenon of osmotic pressure appears for example in biology, in the biological process of living cells. It corresponds to a pressure difference at *thermodynamic equilibrium* between two "compartments" containing solutes of different concentrations.

Imagine two compartments A and B separated by a porous partition which lets solvent 1 through, but not solute 2 (*e.g.* solute 2 is made of particles too large to pass through the holes of a membrane). For example, A could be the interior of a cell bathed in a physiological fluid B.

The partition is not mobile, so there is no volume exchange between the two compartments and the thermodynamic equilibrium does not impose equal pressures: *a priori*, $p_A \neq p_B$. The partition allows heat exchange and therefore the whole system is at the same temperature T. Particles of solvent 1 can be exchanged between A and B, and thus there is equality of the chemical potentials of solvent 1 at equilibrium: $\mu_1(T, p_A, x_2^A) = \mu_1(T, p_B, x_2^B)$, with x_2^A and x_2^B the molar fractions of solute 2 in either compartments. Assuming both are dilute solutions, (8.10) gives

$$\mu_1^0(T, p_A) - RT\, x_2^A = \mu_1^0(T, p_B) - RT\, x_2^B. \tag{8.12}$$

The two chemical potentials can be linked by the fact that in an ordinary liquid, the molar volume v depends little on the pressure (liquids are nearly incompressible). Start from the Gibbs-Duhem relation (4.19): $\partial\mu_1^0/\partial p\big|_T = v$. By integrating this relation between p_A and p_B with v constant, we obtain

$$\mu_1^0(T, p_B) - \mu_1^0(T, p_A) = (p_B - p_A)v. \tag{8.13}$$

By inserting this in (8.12), this leads to:

Frame 8.5 : Osmotic pressure

Two compartments A and B are considered separated by a permeable partition for the solvent (liquid), but do not allow the solute to pass. Then, at thermodynamic equilibrium, we have in the limit of dilute solutions,

$$p_B - p_A = \frac{RT}{v}\left(x_2^B - x_2^A\right). \tag{8.14}$$

The pressure is therefore greater in the compartment with the highest concentration. The pressure difference $p_B - p_A$ is called *osmotic* pressure.

As an example, consider compartment A without any solute, $x_2^A = 0$, and compartment B with $x_2^B = 10^{-3}$. The solvent is water at 300 K. The molar volume of water is v_{water} = [molar mass of water]/[density of water] $= 18\,10^{-3}/10^3 = 1.8\,10^{-5}\,\text{m}^3/\text{mol}$. There is therefore an osmotic pressure of 1.4 bar, which is far from negligible. If the membrane containing A is not very strong, there is a risk of rupture.

Application: Displacement of the transition temperature at fixed pressure

Video 4

At fixed pressure p, suppose that we are looking for the liquid/vapour equilibrium temperature T^* of a dilute solution. T_0 is the liquid/vapour equilibrium temperature of the pure solvent at pressure p; *i.e.* $p = p_{LG}(T_0)$, see frame 7.1. Solute 2 is in the gaseous phase with a molar fraction x_2^G and in the liquid phase with a molar fraction x_2^L, and it is assumed that $x_2^G \ll 1$ and $x_2^L \ll 1$ (dilute solution).

By definition of T^*, the chemical potentials for solvent 1 in the liquid and gaseous phases are equal at this temperature:

$$\mu_1^L(T^*, p, x_2^L) = \mu_1^G(T^*, p, x_2^G).$$

By using (8.10):

$$\mu_1^{L,0}(T^*, p) - RT^* x_2^L = \mu_1^{G,0}(T^*, p) - RT^* x_2^G.$$

Let us expand the chemical potentials of the pure solvent around temperature T_0, in a calculation similar to that of the osmotic pressure. By using, for each phase, the Gibbs-Duhem relation (4.19), we obtain for $\alpha \in \{L, G\}$:

$$\mu_1^{\alpha,0}(T^*, p) \approx \mu_1^{\alpha,0}(T_0, p) + \left.\frac{\partial \mu_1^{\alpha,0}}{\partial T}\right|_p (T^* - T_0) = \mu_1^{\alpha,0}(T_0, p) - s_1^\alpha(T_0, p)(T^* - T_0),$$

where $s_1^\alpha(T_0, p)$ is the molar entropy of the pure solvent in phase α. Using $\mu_1^{L,0}(T_0, p) = \mu_1^{G,0}(T_0, p)$ (because it was assumed that T_0 was the liquid/gas equilibrium temperature of the pure solvent at pressure p) and $s_1^G(T_0, p) - s_1^L(T_0, p) = l_{\text{vap}}/T_0$, with l_{vap} the enthalpy of vaporisation (molar latent heat), see frame 7.3, we find

$$T^* - T_0 = \frac{RT_0^2 \left(x_2^L - x_2^G\right)}{l_{\text{vap}}}. \tag{8.15}$$

If $x_2^G \ll x_2^L$, we find that the liquid/vapour equilibrium temperature at a given pressure increases. In particular, the boiling point (see section 8.4.2 below) also increases. This is *Raoult's law of ebullioscopy.*

We can use the same type of reasoning for solvent *melting* (phase transition between a solid and a liquid). If we assume that $x_2^S \ll x_2^L$, the melting temperature *decreases* according to *Raoult's law of cryoscopy*:

$$T^* - T_0 = -\frac{RT_0^2\, x_2^L}{l_{\text{fusion}}}. \tag{8.16}$$

Take the example of water at atmospheric pressure. If 16 g of salt (NaCl) is added to 1 ℓ of water, the molar fraction of the solute in the liquid is $x_2^L = 10^{-2}$ (one percent solute). For the freezing point, we find a decrease of 1°C. For the vaporisation temperature, we find an increase of 0.3°C.

Complement: derivation of (8.10) and (8.11)

In this optional supplement, a model is described to understand the limit of the dilute solutions of frame 8.4.

Let n_1 moles of solvent and n_2 moles of solute be in volume V at temperature T. If the interactions between species 1 and 2 were completely neglected, the free energy would be given, as in (8.4) by

$$F(T,V,n_1,n_2) = F_1(T,V,n_1) + F_2(T,V,n_2) \qquad \text{(without interaction)},$$

with F_1 and F_2 the free energies of the two compounds alone (considered as pure). Here, we suppose that n_2 is small enough that species 2 alone can be considered as an ideal gas: F_2 in the above equation is therefore that of an ideal gas. It is now necessary to take into account the interactions between the particles of species 1 and those of species 2. The particles of species 2 are isolated. Every single one of them interacts with the particles of species 1 surrounding it and is far from all other particles of species 2. This means that the interaction term must be proportional to the number of particles of species 2, and therefore proportional to n_2. So we write, using the extensivity property to simplify the dependency in n_1 and V,

$$F(T,V,n_1,n_2) = F_1(T,V,n_1) + F_{\text{ideal gas}}(T,V,n_2) + n_2 f_{\text{int}}\Big(\frac{n_1}{V},T\Big) \qquad \text{(with interaction)}, \quad (8.17)$$

where f_{int} is an unspecified function and where F_2 has been replaced by the free energy of an ideal gas. Let us differentiate this equation with respect to n_1:

$$\mu_1(T,V,n_1,n_2) = \mu_1^0(T,V,n_1) + \frac{n_2}{V} f'_{\text{int}}\Big(\frac{n_1}{V},T\Big). \qquad (8.18)$$

The part on the left-hand side is the chemical potential that we are trying to calculate. μ_1^0 is the chemical potential of species 1 alone (pure) in volume V. We used the abusive notation f'_{int} to designate the derivative of f_{int} with respect to its first variable.

We want to obtain the chemical potential as a function of the pressure. We have

$$\mu_1(T,p,x_2) = \mu_1(T,V,n_1,n_2),$$

where p is the pressure of the *solution* corresponding to the parameters T, V, n_1, n_2 and where $x_2 = n_2/(n_1+n_2) \approx n_2/n_1$ is the molar fraction of the solute. Similarly, we write

$$\mu_1^0(T,p_1) = \mu_1^0(T,V,n_1),$$

where p_1 is the pressure of the *solvent alone* corresponding to the parameters T, V, n_1. Caution, p_1 is close, but not quite equal to p. Using a Gibbs-Duhem relation, we have as in (8.13)

$$\mu_1^0(T,p_1) \approx \mu_1^0(T,p) + (p_1 - p)\frac{V}{n_1},$$

where the molar volume of the solvent V/n_1 was noted v in (8.13). Putting the last three equations in (8.18), we find

$$\mu_1(T,p,x_2) \approx \mu_1^0(T,p) + (p_1 - p)\frac{V}{n_1} + \frac{n_2}{V} f'_{\text{int}}\Big(\frac{n_1}{V},T\Big). \qquad (8.19)$$

We are now trying to estimate p_1. For this, we just need to use $p = -\partial F/\partial V$; deriving (8.17) with respect to V and multiplying by -1, we get

$$p = p_1 + p_2 + \frac{n_1 n_2}{V^2} f'_{\text{int}}\Big(\frac{n_1}{V},T\Big),$$

where p and p_1 have already been defined and where p_2 is the pressure that the solute alone would have in volume V. Using this relationship between pressures, (8.19) can be simplified:

$$\mu_1(T,p,x_2) \approx \mu_1^0(T,p) - p_2\frac{V}{n_1}.$$

But p_2 is the pressure of the solute considered alone, *i.e.* the pressure of an ideal gas: $p_2V = n_2RT$. By writing $n_2/n_1 \approx x_2$, we find (8.10).

Let us calculate μ_2. We differentiate (8.17) with respect to n_2 and we find

$$\mu_2(T,p,x_2) = \mu_{\text{ideal gas}}(T,p_2) + f_{\text{int}}\Big(\frac{n_1}{V},T\Big) = RT\ln(p_2) + f(T) + f_{\text{int}}\Big(\frac{n_1}{V},T\Big), \tag{8.20}$$

where (8.8) was used to express the chemical potential of the ideal gas. The volume of the solution is a function of p, T, n_1 and n_2. In fact, as $n_2 \ll n_1$, we have to the first order by extensivity $V = V(p,T,n_1,n_2) \approx V(p,T,n_1,0) = n_1v(p,T)$. Then $p_2 = n_2RT/V \approx n_2RT/[n_1v(p,T)] \approx x_2RT/v(p,T)$. Putting these expressions of p_2 and V in (8.20), we find the expected result (8.11) with $\Psi(T,p) = f(T) + f_{\text{int}}\big(\frac{1}{v(p,T)},T\big) + RT\ln[RT/v(p,T)]$.

8.3 Phase diagram of binary solutions

In this section, we consider a binary solution $c = 2$ undergoing a transition: the number of phases goes from $\phi = 1$ to $\phi = 2$.

8.3.1 Isobar diagram

We consider a binary solution under one or two phases.

When there is only one phase, the Gibbs' phase rule (see frame 8.1) tells us that there are three independent intensive parameters p, T and x_2, the molar fraction of species 2 in the phase considered. This means that, at fixed p and T, x_2 is not fixed.

When there are two phases (*e.g.* liquid and vapour), x_2 can always be defined as the ratio between the total number of moles of species 2 and the total number of moles. However, the Gibbs' phase rule tells us that there are only two independent intensive parameters: if we fix p and T, the molar fractions of species 2, $x_2^L(p,T)$ and $x_2^G(p,T)$, in either phases are fixed. These fractions are in general different from x_2.

In all cases, the state of the system at fixed p is represented as a point in a certain region of the (x_2,T) diagram. When there is only one phase, the x-coordinate x_2 is the molar fraction of species 2 in that single phase. When there are two phases, the x-coordinate x_2 no longer represents the molar fraction of a given phase.

A typical example of a system at fixed p is shown in Figure 8.1. In the presence of two phases, in the (x_2,T) diagram, the molar fractions $x_2^L(p,T)$ and $x_2^G(p,T)$ that have just been defined correspond to two curves.

Depending on the total molar fraction x_2 of species 2 and of the temperature, the system can be:

- in the high temperature region I: there is only the gas phase and $x_2^G = x_2$;
- in the low temperature region II: there is only the liquid phase and $x_2^L = x_2$;
- in the intermediate region, between the two curves: there is coexistence of the two phases.

To better understand what is happening, let us imagine that we start from a liquid with a molar fraction x_2 of species 2 (point A in Figure 8.2) and that we heat (at constant pressure).

The temperature increases, but x_2 remains constant: in the figure, the state is described by a point that rises vertically until it touches the change of state line where the first gas bubble appears (point B). x_2^G, the molar fraction of species 2 in the gas bubble, is obtained by plotting the horizontal line of y-coordinate corresponding to the temperature at point

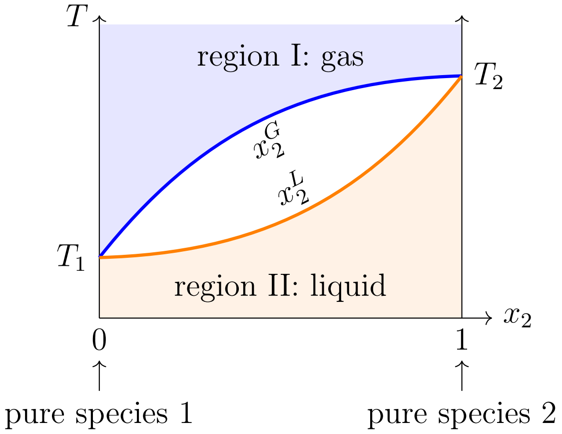


Figure 8.1: An isobar phase diagram of a typical binary solution. For the pressure considered, T_1 is the liquid/gas coexistence temperature of species 1 alone and T_2 is the liquid/gas coexistence temperature of species 2 alone.

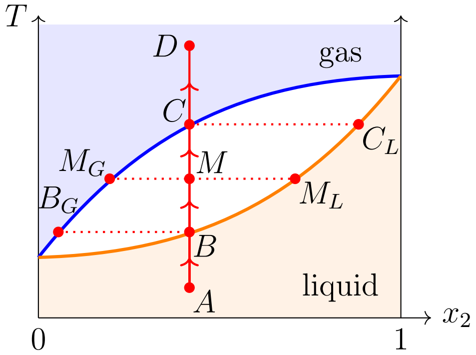


Figure 8.2: Heating a liquid binary solution.

B which intersects the curve $x_2^G(T)$ at point B_G. Then, by increasing the temperature, the values of the molar fractions of species 2 in the gas and the liquid are obtained in the same way. At point M, they are the x-coordinate of point M_G, equal to x_2^G, and that of point M_L, equal to x_2^L. At point C only the last drop of liquid remains, with the molar fraction x_2^L for species 2 corresponding to the x-coordinate of point C_L. At higher temperatures, the system is completely in the gaseous phase (point D). Remark: contrary to what happens for a pure substance, the temperature of the binary mixture changes during the phase change.

For a system composed of n moles in the liquid/gas coexistence region, for example at point M of Figure 8.2, it is easy to calculate the number of moles n_L in the liquid phase. On the one hand, the total number of moles of species 2 is given by $x_2 n$ and on the other hand by $x_2^L n_L + x_2^G(n - n_L)$, where $n - n_L$ is of course the number moles n_G in the gas phase. We obtain the *lever rule*:

Frame 8.6 : Lever rule

Let a binary solution have a molar fraction x_2 of species 2 at equilibrium under two phases (liquid and gas). Then the molar fraction n_L/n of particles in the liquid phase is given by

$$\frac{n_L}{n} = \frac{x_2 - x_2^G}{x_2^L - x_2^G} = \frac{\text{distance between } M \text{ and } M_G}{\text{distance between } M_L \text{ and } M_G}, \tag{8.21}$$

where the points M_L, M and M_G indicated on Figure 8.2 have x_2^L, x_2 and x_2^G for x-coordinate, respectively.

Application: distillation

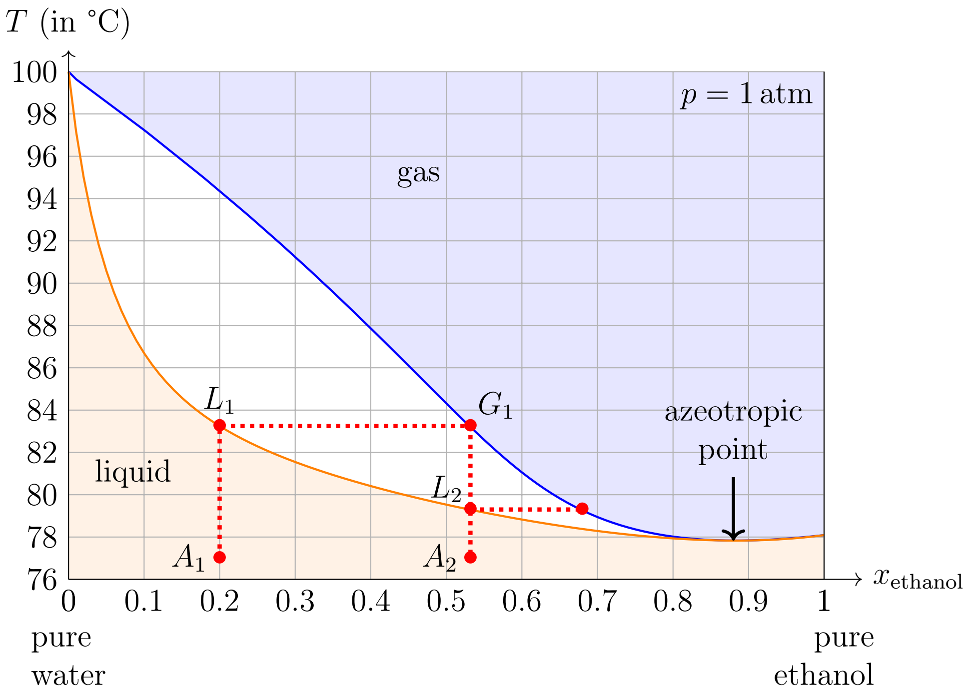


Figure 8.3: Principle of distillation.

Figure 8.3 represents the isobaric phase diagram under atmospheric pressure of a water-ethanol mixture. Suppose we initially have a liquid with a molar fraction of ethanol $x_{\text{ethanol}} = 0.2$ (point A_1 on Figure 8.3). The solution is heated to the point L_1; the vapour thus formed, with a molar fraction of ethanol x^G_{ethanol} (x-coordinate of point G_1) greater than the initial value, is removed. It passes through a condenser (which cools it down) where it is converted to a liquid, but with the same molar fraction x^G_{ethanol} richer in ethanol with respect to the original liquid! This new enriched solution (point A_2) can be heated again to increase the proportion of ethanol, *etc.* Concentrated alcohol (eau-de-vie, spirits) can be obtained through this process. Nevertheless, the water-ethanol solution has one particularity: the *azeotropic* point, see Figure 8.3. At this point, the water/ethanol solution boils at a fixed temperature and with a constant composition. In practice this limits distillation.

8.4 Degree of humidity, evaporation, boiling

Video 5

8.4.1 Evaporation

Evaporation is the process by which a liquid gradually vaporises through its free surface. If the evaporation occurs in an atmospheric environment, the gaseous phase can be considered as a solution of pure substances. Consequently, as we shall see, the evaporation can be observed at temperatures much lower than that of the change of state of the same pure substance at the same pressure: under atmospheric pressure, water can indeed evaporate at 20°C.

Let us study the evaporation of a given substance (for example water, or alcohol) in the presence of an atmosphere at (total) pressure p_{atm}. The equilibrium condition between the liquid and gaseous phases of the studied substance is always $\mu_{\mathrm{G}} = \mu_{\mathrm{L}}$, but the expression of the chemical potentials in the solutions is complex. To simplify the problem, we will make some assumptions.

- The gas phase is a mixture of ideal gases, so that according to (8.7), the chemical potential of the substance is written

$$\mu_{\mathrm{G}}(T, p_{\mathrm{atm}}, x) = \mu_{\mathrm{G}}^0(T, p_{\mathrm{vapour}}) = \mu_{\mathrm{G}}^0(T, x p_{\mathrm{atm}}), \tag{8.22}$$

  where μ_{G}^0 is the expression of the chemical potential for pure gaseous substances and $p_{\mathrm{vapour}} = x p_{\mathrm{atm}}$ its partial pressure in the solution, x being its molar fraction.
- The dissolution of the gases from the atmosphere into the liquid is neglected, the latter being therefore considered as pure. Then, moving away from the critical point, we neglect the molar volume of the liquid with respect to that of the gas. This hypothesis means that we neglect the pressure dependence of the chemical potential of the liquid, and thus:

$$\mu_{\mathrm{L}} = \mu_{\mathrm{L}}^0 = \mu_{\mathrm{L}}^0(T). \tag{8.23}$$

  where μ_{L}^0 is the expression of the chemical potential for the pure liquid substance.

In these conditions, the equilibrium condition $\mu_{\mathrm{G}} = \mu_{\mathrm{L}}$ becomes $\mu_{\mathrm{G}}^0(T, p_{\mathrm{vapour}}) = \mu_{\mathrm{L}}^0(T)$ which, compared with (7.2) and (7.3), leads to

$$p_{\mathrm{vapour}} = p_{\mathrm{s}}(T) \quad \Longrightarrow \quad x = \frac{p_{\mathrm{s}}(T)}{p_{\mathrm{atm}}} = x_{\mathrm{s}}(T, p_{\mathrm{atm}}), \tag{8.24}$$

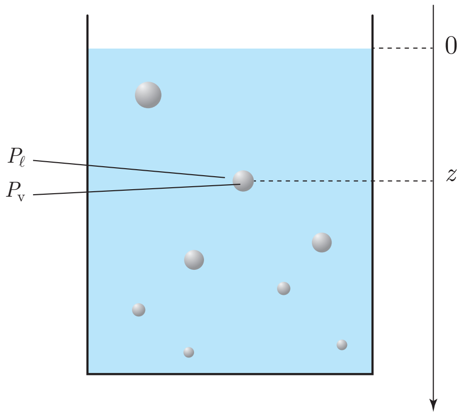
where $p_s(T)$ is the saturating vapour pressure at temperature T, that is the pressure of the liquid/gas equilibrium for a pure substance. For example, $p_{\mathrm{s}}(20°\mathrm{C}) = 0.023\,\mathrm{bar}$ for water. At equilibrium, at atmospheric pressure $p = 1$ bar and at this temperature of 20°C, water evaporates with a molar fraction of 2.3 % of vapour. At $T = 0\,°\mathrm{C}$, $p_{\mathrm{s}}(0°\mathrm{C}) = 0.006\,\mathrm{bar}$ the molar fraction drops to 0,6 %. These values show that if, when at equilibrium, the air charged with moisture cools down, the excess vapour liquefies in the form of fine droplets, forming fog or mist.

When evaporation takes place in an open environment, the vapour produced by the liquid is diluted or removed, so that equilibrium is never reached and the evaporation continues until the liquid dries out. Outside of equilibrium, the *relative humidity* ϕ of the (supposedly homogeneous) gas phase is defined as the ratio of the observed vapour density $x = p_{\mathrm{vapour}}/p_{\mathrm{atm}}$ to the saturation (equilibrium) vapour density $x_{\mathrm{s}}(T, p_{\mathrm{atm}}) = p_{\mathrm{s}}(T)/p_{\mathrm{atm}}$:

$$\phi = \frac{x}{x_\mathrm{s}} = \frac{p_\mathrm{vapour}}{p_\mathrm{s}(T)} \leqslant 1. \tag{8.25}$$

The evaporation of an element of mass $\mathrm{d}m$ from the liquid phase, at a given temperature and pressure, is done with a heat transfer towards the liquid $\delta Q = \mathrm{d}H = \mathrm{d}m\, L_\mathrm{v}$; this heat is necessarily transferred by the rest of the system. The evaporation of a liquid thus causes the cooling of its environment. This mechanism is used by the human body to regulate its temperature in case of hot weather or high body temperatures through the evaporation of perspiration. This evaporation is all the more effective when the atmosphere is not saturated with water, *i.e.* that the relative humidity is low, hence the impression of greater heat (temperatures) in a humid environment.

8.4.2 Boiling



Schematic of boiling in a liquid.

Boiling is a manifestation of vaporisation with the tumultuous creation of bubbles in the liquid. It is a daily phenomenon, but very complex because of the multiple effects that intervene. First of all, it must be pointed out that a boiling liquid is not in thermodynamic equilibrium: its state varies rapidly with time and, moreover, it has a temperature gradient as well as convection mouvements.

Boiling of a liquid is usually done in atmospheric conditions (in contact with air), so the phases do not consist of a single pure substance: there are dissolved gases in the liquid, and the vapour released by the vaporisation mixes with the air. For simplicity, evaporation can be neglected, so that vaporisation occurs essentially at the level of the bubbles. At the initial stages of boiling, these bubbles contain a mixture of the vapour with other gases released by the liquid. However, these released gases (initially dissolved) are quickly a minority and we can consider that the bubbles contain only pure vapour. The problem is thus reduced to that of a pure substance.

As a first approximation, the reasoning is as follows: the atmosphere, the liquid and the bubbles in the liquid are all at (about) the same pressure. At the bubble level, the equilibrium condition of the chemical potential of the vaporising substance remains accurate, and the pressure of the system must be equal to the saturation vapour pressure $p_s(T)$ of the substance. The boiling temperature is thus obtained by

$$p_s(T) = p_\mathrm{atm}$$

with p_atm the pressure of the atmosphere above the system.

In reality, the situation is more complex: if, despite convection, the hydrostatic law is admitted; then the pressure in the liquid at depth z must be written:

$$p_\mathrm{L}(z) = p_\mathrm{atm} + \rho g z,$$

ρ being the density of the liquid and g the acceleration of gravity. In addition, the surface $\mathcal{S}$ of the liquid/gas interface plays a significant role in the parameters of the system, which adds a term $\sigma\, \mathrm{d}\mathcal{S}$ in the thermodynamic identity, where σ is the *surface tension.* Admitting that the bubbles are spherical, it can be shown that the pressure p_{bubble} inside the bubble is greater than the pressure $p_{\text{L}}(z)$ of the liquid; more precisely

$$p_{\text{bubble}} - p_{\text{L}}(z) = \frac{2\sigma}{r} \tag{8.26}$$

(Law of Laplace), where r is the radius of the bubble. The condition of existence of the bubbles $p_{\text{bubble}} = p_{\text{s}}(T)$ then becomes

$$p_{\text{s}}(T) = p_{\text{atm}} + \rho g z + \frac{2\sigma}{r}.$$

In this formula, one should also take into account the temperature gradient (*i.e.* $T = T(z)$), the dispersion and variation of the radii of bubbles when they rise, and even the fact that the amount of vapour in the bubbles increases. The quantitative exploitation of this result is therefore very complex. Nevertheless, it is qualitatively inferred that boiling can be observed over a temperature range T in the liquid and a pressure range p_{atm} above the liquid, following the law in $p_{\text{s}}(T)$, the pressure p_{atm} always being lower than the value of $p_{\text{s}}(T)$ at the same temperature.