

# Principles of Thermal Physics

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# 1 Introduction

Thermodynamics aims at describing global properties of macroscopic systems, ignoring their microscopic structure.

## 1.1 Pressure

Consider an elementary area  $d\vec{A}$  in a fluid (the arrow denotes the direction perpendicular to the area). The force  $d\vec{F}$  applied on one side of this area by the fluid is proportional to  $d\vec{A}$  and the pressure  $P$  is defined as

$$d\vec{F} = Pd\vec{A}.$$

The pressure is an isotropic quantity (independent of the orientation of the area). If we consider an infinitesimal parallelepipedic volume (dimensions  $dx$ ,  $dy$  and  $dz$ ), the  $x$ -component of the force applied on the volume is

$$dF_x = P(x, y, z)dydz - P(x + dx, y, z)dydz = -\frac{\partial P}{\partial x}dxdydz.$$

The same holds for the other components, such that the force per unit volume  $d\tau = dxdydz$  due to the pressure is given by

$$\frac{d\vec{F}}{d\tau} = -\vec{\nabla}P. \quad (1)$$

The pressure unit is the Pascal:  $1 Pa = 1 N.m^{-2}$ .

## 1.2 Temperature

Zeroth Law: *Two systems in thermal equilibrium with a third one are in thermal equilibrium between themselves.*

This Law is the basis of our concept of temperature and leads to different empirical methods to measure it. The 'official' way to define the temperature is the following. Consider a gas in a volume  $V$  with a pressure  $P$ . We see experimentally that the product  $PV$  goes to a value which depends only on the temperature when  $P \rightarrow 0$ , value which is independent of the gas. If we make this experiment in two different situations  $A$  and  $B$ , we define the absolute temperatures  $T_A$  and  $T_B$  by the ratio

$$\frac{(PV)_A}{(PV)_B} = \frac{T_A}{T_B},$$

and the value  $T_0 = 273,16K$  (unit: Kelvin) for the triple point of water.

### 1.3 Transformation of a system

A state variable is a parameter used to describe the macroscopic state of a system. This variable is extensive if it is proportional to the volume and intensive if it is independent of the volume. The equation of state gives the relation between the different state variables (for example: pressure, volume and temperature), relation which defines the system.

A system is at the equilibrium if each of its state variable has a defined value which does not evolve in time.

A reversible transformation consists in a series of equilibrium states infinitesimally close, for the system *and* for the surroundings. In a reversible process, the system and the surroundings should be able to go backwards in time, passing through the same series of equilibrium states.

An irreversible transformation is a transformation which does not satisfy the above criteria. During an irreversible transformation, we cannot define the state variables since the system does not pass through equilibrium states.

In practice, a reversible transformation is a process in which the evolution of the state variables is 'slow enough' compared to the typical relaxation times of the system.

### 1.4 Work and Heat

Consider a gas under the external pressure  $P_{ext}$ . In an infinitesimal change of volume  $dV$ , the external pressure forces have the work

$$dW = -P_{ext}dV,$$

where by convention we count  $dW > 0$  when the gas gets work from the surroundings and  $dW < 0$  when the gas gives work to the surroundings. In a reversible process, where the equilibrium state is reached at each step and the internal pressure balances the external one ( $P_{ext} = P$ )

$$dW_{rev} = -PdV \quad (\text{reversible process}).$$

Let us consider another example of work. Suppose an interface liquid/gas of area  $A$ . It is shown experimentally that a change in this area needs the work

$$dW = \gamma dA,$$

where  $\gamma$  is the surface tension. As an application, we can compute the difference  $\Delta P$  between the pressure inside a drop of liquid of radius  $R$  and the pressure outside the drop. In a change of radius, the work of the surface tension is

$$dW_1 = \gamma d(4\pi R^2),$$

and the work of the pressure forces is

$$dW_2 = -\Delta P d\left(\frac{4}{3}\pi R^3\right).$$

The surface tension has the tendency to shrink the drop and the inside pressure to increase the radius. The equilibrium is obtained when  $dW_1 + dW_2 = 0$ , such that

$$\Delta P = \frac{2\gamma}{R}.$$

The heat  $Q$  is the non-mechanical transfer of energy due to a difference of temperature between two systems. It flows through a system by molecular agitation, from one to the next.

An *adiabatic* process is a process without heat exchange  $Q = 0$ . In reality, there is no real adiabatic process, but we can make this approximation if the heat transfers are slow enough compared to the typical time scale of the process.

As well as for the work, the heat is defined *during a transformation* and does not characterize the state of a system.

## 2 First Law

### 2.1 Internal Energy

The internal energy of a system is the sum of the energies of the different degrees of freedom.

In the example of a gas, the total energy consists in the different kinetic energies of the particles (translation, rotation, vibration) and the potential energies corresponding to the interaction between particles.

For a general system, we expect the conservation of the energy and assume the First Law: *To any system corresponds a state function  $U$  called the internal energy. The change of  $U$  in a transformation is equal to the energy (work and heat) exchanged with the surroundings.*

A state function is a function of the parameters which define the state of the system: it is independent of the transformations which led to the given state (see fig.1).

The First Law reads quantitatively

$$\Delta U = W + Q,$$

and for an infinitesimal transformation

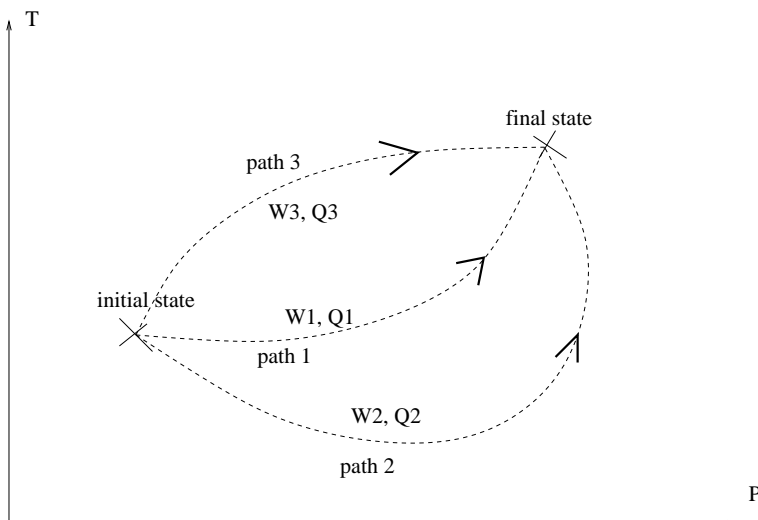


Figure 1: Different transformations connecting the initial and the final states. Work and heat are different in each case:  $W_1 \neq W_2 \neq W_3$  and  $Q_1 \neq Q_2 \neq Q_3$ , but the change in internal energy is independent of the path:  $\Delta U = U(\text{final state}) - U(\text{initial state}) = W_1 + Q_1 = W_2 + Q_2 = W_3 + Q_3$ .

$$dU = \delta W + \delta Q.$$

We note  $dU$  since it corresponds to the differential of a function and  $\delta W$  or  $\delta Q$  since these correspond to infinitesimal energy transfers and *not* to differentials of functions: they depend on the path (in the parameter space) that the system followed to go from one state to another.

For a gas, the change of internal energy is

$$dU = -P_{ext}dV + \delta Q, \quad (2)$$

and for a reversible process, where  $P_{ext} = P$  during the transformation,

$$dU_{rev} = -PdV + \delta Q \quad (\text{reversible process}).$$

From Eq.(2), we obviously have the following property: the change in internal energy in a process with constant volume is equal to the heat exchanged with the surroundings, i.e.

$$\Delta U = Q \quad (V=\text{Constant}).$$

Finally, we define the heat capacity at constant volume by

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V.$$

## 2.2 Enthalpy

Many processes occur under constant pressure. Thus it is convenient to introduce another state function with the dimension of an energy: the enthalpy  $H$  defined by

$$H = U + PV.$$

We will see in section 6 that  $H$  is a Legendre transform of  $U$ . For the moment, we can say that if the pressure is constant  $P = P_0$ ,

$$\Delta H = \Delta U + P_0\Delta V = -P_0\Delta V + Q + P_0\Delta V = Q,$$

such that the change in enthalpy is equal to the heat exchanged with the surroundings:

$$\Delta H = Q \quad (P=\text{Constant}).$$

We define the heat capacity at constant pressure  $C_P$  by

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P.$$

As an application, consider a system 1 (mass  $m_1$ , initial temperature  $T_1$  and heat capacity per unit mass  $c_1$ ) put in contact with a system 2 (mass  $m_2$ , initial temperature  $T_2$  and heat capacity per unit mass  $c_2$ ), such that they can exchange heat only (at constant pressure) and they are isolated from the surroundings. We can compute the final temperature  $T_0$  by noting that the total enthalpy is conserved:

$$0 = \Delta H_1 + \Delta H_2 = m_1c_1(T_0 - T_1) + m_2c_2(T_0 - T_2),$$

such that finally

$$T_0 = \frac{m_1c_1T_1 + m_2c_2T_2}{m_1c_1 + m_2c_2}.$$

Thus the final temperature is the weighted average of the initial temperatures, the weights being the heat capacities  $C_i = m_i c_i$  ( $i = 1, 2$ ).

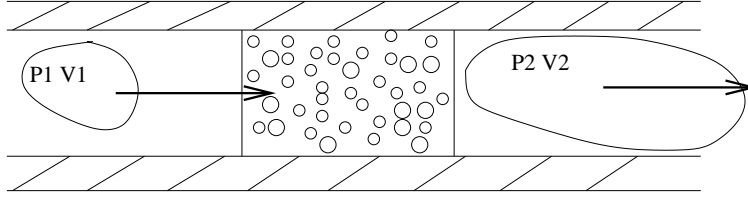


Figure 2: The gas flows adiabatically through a porous plug and sees its pressure drop.

## 2.3 Joule-Kelvin throttling process

This process is a well-known example where the enthalpy is conserved. Suppose that a gas of initial pressure  $P_1$  passes through a porous plug inside a cylinder, in an adiabatic way (see fig.2). The plug induces a pressure drop such that the gas emerges with pressure  $P_2 < P_1$ . So as to describe quantitatively this *irreversible* process, imagine the following equivalent process: a given quantity of gas, of volume  $V_1$ , is compressed in the plug by a piston under the external constant pressure  $P_1$  and, when emerging out of the plug, pushes another piston with constant pressure  $P_2$  so as to arrive in the final state, with volume  $V_2$ . The work exchanged with the surroundings is  $W = P_1V_1 - P_2V_2$  and the heat  $Q = 0$ , such that the first law reads

$$U_2 - U_1 = Q + W = P_1V_1 - P_2V_2,$$

which can be written  $H_2 = H_1$ : the process is isenthalpic. Note that this property holds for *any* gas: it is independent of the equation of state that defines the system.

## 3 Ideal gas

### 3.1 Definition

From a macroscopic point of view, an ideal gas can be defined by its equation of state:  $PV = \text{Constant} \times T$ . Since  $P$  and  $T$  are intensive variables and  $V$  is extensive, the constant must be extensive: it is proportional to the number of moles  $n$ , such that

$$PV = nRT.$$

A mole contains  $\mathcal{N} = 6.0221 \times 10^{23}$  particles and  $R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ .

As an example, we can compute the pressure decrease in an ideal gas of uniform temperature  $T$ , in a uniform gravitation field  $g$ . Consider a slice of gas between the altitude  $z$  and  $z + dz$ , of mass  $dm$  and occupying the volume  $dV$ . Its density  $\rho(z)$  satisfies

$$\rho(z) = \frac{dm}{dV} = M \frac{dn}{dV} = M \frac{P(z)}{RT},$$



where  $M$  is the mass of a mole and  $dn$  the number of moles. Using the result (1), the equilibrium of the slice of gas reads

$$\frac{dP}{dz} + \rho(z)g = 0,$$

such that

$$P(z) = P_0 \exp \left\{ -\frac{Mg}{RT} z \right\},$$

with  $P_0 = P(0)$ .

### 3.2 Phenomenological derivation of the kinetic pressure

From the microscopic point of view, the essential property of an ideal gas is that there are no interactions between the particles.

We derive here an expression of the pressure in terms of the mean quadratic velocity of the particles of the gas, using a phenomenological microscopic description.

Let us consider an area  $A$  of the container of the gas, perpendicular to the  $x$ -axis (see fig.3). A particle hitting  $A$  induces a force  $\vec{f} = -md\vec{v}/dt$  where its velocity decreases from  $\vec{v}$  to 0 during the time  $dt$ . In the time  $\Delta t$ , the particles with velocity of component  $v_x$  along the  $x$ -axis will give the force  $F_x$  with

$$\Delta t F_x = - \sum \int_{v_x}^0 m dv = \sum m v_x,$$

where the sum runs over the particles. If  $N$  is the total number of particles in the gas of total volume  $V$ , the number of particles hitting the area  $A$  in the time  $\Delta t$  is  $A|v_x|\Delta t N/V$ . The force  $F_x$  is then

$$F_x = \frac{1}{2} m v_x^2 A \frac{N}{V},$$

where the factor 1/2 is present so as not to count the particles with velocity  $-\vec{v}$ . The reemission of the particle in the gas involves a new force  $F'_x = F_x$  (reaction of the container), such that the pressure is

$$P = \frac{F_x + F'_x}{A} = m \frac{N}{V} \overline{v_x^2},$$

where  $\overline{v_x^2}$  is the mean squared velocity. The isotropy tells us that  $\overline{v_x^2} = (\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2})/3 = (v^*)^2/3$ , where  $v^*$  is the mean quadratic velocity. The pressure finally satisfies

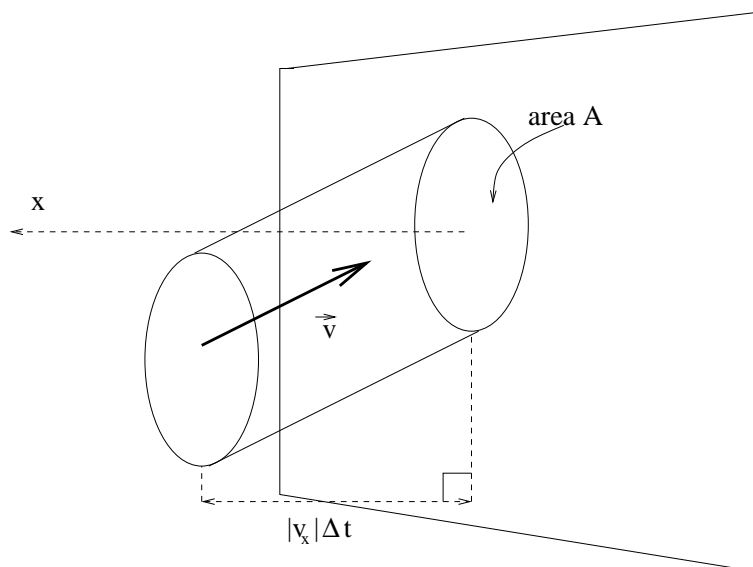


Figure 3: Particles hitting the wall of the container.

$$PV = \frac{mN(v^*)^2}{3}, \quad (3)$$

and the ideal gas equation of state thus gives

$$v^* = \sqrt{\frac{3RT}{M}}. \quad (4)$$

The result (4) tells us that *the mean quadratic velocity of the particles depends on the temperature only*. This important point will be used for the energetic properties of an ideal gas.

### 3.3 Internal energy

We have seen that the mean quadratic velocity of the particles in an ideal gas is a function of the temperature only. Consider now the internal energy of a monoatomic ideal gas. This energy consists only in the translation kinetic energy of the particles: there is no rotation or vibration (monoatomic) and no potential energy (ideal gas), thus

$$U = \sum \frac{1}{2}m(v^*)^2 = \frac{1}{2}nM(v^*)^2 = \frac{3}{2}nRT.$$

The essential result is that *U depends on the temperature only*. For a general ideal gas, this property is still valid and we will show this in the chapter 6. It is called the first Joule law. The enthalpy  $H = U + PV = U + nRT$  also depends on the temperature only: this is

the second Joule law. As a consequence, an ideal gas does not see its temperature change in a Joule-Kelvin throttling process.

We have also

$$C_V = \frac{dU}{dT} \quad C_P = \frac{dH}{dT},$$

and  $C_V$  and  $C_P$  are functions of  $T$  only.

From their definition and the relation  $H = U + nRT$ , we obviously have

$$C_P - C_V = nR, \tag{5}$$

which is called the Mayer relation. Finally, we define the ratio

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

which is larger than 1, since  $C_P > C_V$  (see Eq.(5)).

### 3.4 Isothermic compression

Let us see an example of isothermic transformation. Suppose a reversible process at constant temperature  $T$ , where an ideal gas is compressed from a volume  $V_1$  to a volume  $V_2$ . The work is given by

$$W = - \int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \left( \frac{V_1}{V_2} \right) = nRT \ln \left( \frac{P_2}{P_1} \right).$$

For the temperature to be constant, one must check that the compression is slow enough so that the heat can flow through the system. Anyway, the reversibility implies that the process must be slow compared to the typical time of energy exchanges.

In such a process, since  $T=\text{Constant}$ , the internal energy does not change  $\Delta U = 0$ , such that the heat exchanged with the surroundings is  $Q = -W$ .

### 3.5 Adiabatic compression

In the situation of an adiabatic compression, the transformation must be quick enough, so that the approximation  $Q = 0$  is valid. Still, the compression will be supposed reversible. The equation of state implies

$$\frac{dP}{P} + \frac{dV}{V} = \frac{dT}{T}. \tag{6}$$

But we also have  $dU = C_V dT = -PdV$ , such that

$$\frac{dT}{T} = -\frac{P}{C_V T} dV = -\frac{nR}{C_V} \frac{dV}{V},$$

and therefore, using Eq.(6),

$$\frac{dP}{P} + \left(1 + \frac{nR}{C_V}\right) \frac{dV}{V} = 0.$$

With the Mayer relation (5), we obtain

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0,$$

which integrates as (we suppose that  $\gamma$  is constant)

$$PV^\gamma = \text{Constant} \quad (\text{adiabatic and reversible}).$$

As a consequence, in a Clapeyron diagram ( $P, V$ ), the slope of an adiabatic transformation is larger (in absolute value) than the slope of an isothermic transformation ( $PV = \text{Constant}$ ) since  $\gamma > 1$ .

The work during such a compression between the states  $(P_1, V_1)$  and  $(P_2, V_2)$  is

$$W = -\int_{V_1}^{V_2} P dV = -P_2 V_2^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma},$$

such that

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \quad (\text{adiabatic}). \quad (7)$$

Note now that since  $Q = 0$ , we have  $\Delta U = W$  and thus *in this particular case*  $W$  is a state function, independent of the transformation between the initial state 1 and the final state 2. Therefore Eq.(7) is valid for *any* adiabatic transformation of an ideal gas.

### 3.6 Carnot cycle

A system describes a cycle when it comes back to its initial state. In this case, the important point is that the internal energy, being a state function, does not vary:

$$\Delta U_{\text{cycle}} = 0.$$

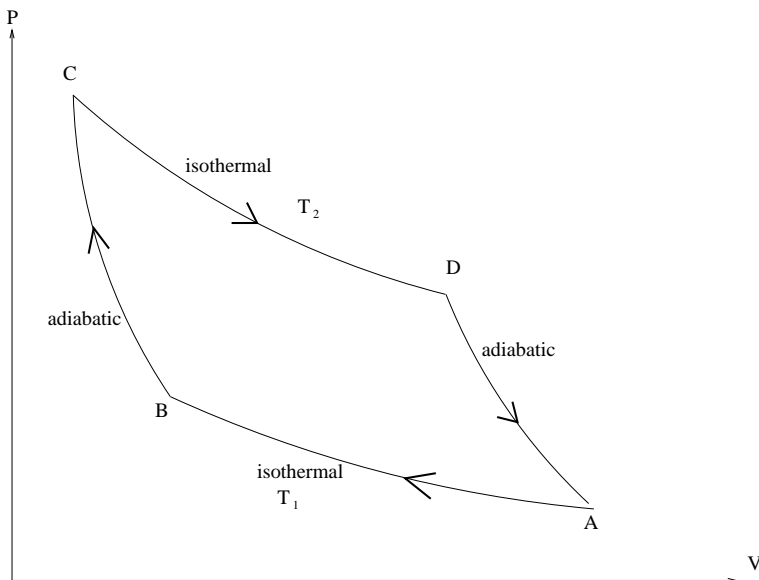


Figure 4: An example of Carnot cycle in the Clapeyron diagram ( $P, V$ ). Heat is exchanged with the surroundings during the isothermic stages AB and CD only. The cycle is followed clockwise, which means that it describes an engine.

In the Clapeyron diagram, a cycle goes clockwise if  $W < 0$  (case of the thermal engines) and goes in the trigonometric sense if  $W > 0$ .

A Carnot cycle is a reversible cycle followed by a gas in contact with two heat sources. We will see the Carnot cycles more generally in section 5 but consider now the case of an ideal gas operating under two isothermic transformations linked by two adiabatic transformations (see fig.4).

Let  $T_1$  and  $T_2$  be the two temperatures ( $T_2 > T_1$ ) of the isothermic processes with the associated heats  $Q_1 < 0$  and  $Q_2 > 0$ , and  $W$  be the total work. We have

$$0 = \Delta U = W + Q_1 + Q_2.$$

We define the efficiency  $\eta$  by the ratio of the work obtained by the user of the engine (this work is negative since the gas gives it to the surroundings) over the heat taken from the hot source (of temperature  $T_2$ ) which represent the energy coming from the chemical reactions during the explosion in the engine. We have then

$$\eta = -\frac{W}{Q_2} = 1 + \frac{Q_1}{Q_2}$$

To compute this efficiency, we need  $Q_1$  and  $Q_2$ . During the isothermic transformations, the internal energy does not vary (ideal gas) so that  $Q = -W$ . Consider the isothermic compression at the temperature  $T_1$  from the state  $(P_A, V_A)$  to the state  $(P_B, V_B)$ ,  $P_B > P_A$ . We have

$$Q_1 = + \int_{V_A}^{V_B} P dV = nRT_1 \ln \frac{V_B}{V_A} = nRT_1 \ln \frac{P_A}{P_B},$$

which is negative. For the other isothermic process, between the states  $(P_C, V_C)$  and  $(P_D, V_D)$  at temperature  $T_2$ , we have

$$Q_2 = nRT_2 \ln \frac{P_C}{P_D},$$

which is positive. These two processes are linked by adiabatic transformations, such that

$$P_B V_B^\gamma = P_C V_C^\gamma \quad \text{and} \quad P_A V_A^\gamma = P_D V_D^\gamma,$$

and therefore, when using the equation of state,  $P_C/P_D = P_B/P_A$ . Finally, the efficiency is

$$\eta = 1 - \frac{T_1}{T_2}.$$

We will see in section 5 that this efficiency is actually independent of the gas and that it is the maximum efficiency that one can obtain in a real process which is not reversible.

## 4 Second Law

The approach to the Second Law which is presented here does not follow the historical developments, but is more convenient from the formal point of view.

### 4.1 Motivations

We have seen the notion of reversibility. Obviously, many phenomena are not reversible (diffusion of a drop of ink in water, cooling of a hot metallic rod in cold water, free expansion of a gas,...) for which we never see the processes evolve backwards in time. Still, this would not invalidate the conservation of energy. Thus the First Law is not enough to describe these processes. To complete the study of macroscopic systems and give an 'arrow' in time to the irreversible processes, we assume the Second Law: *To any system corresponds an extensive state function  $S$  called the entropy, such that  $S$  increases during a transformation of an isolated system and reaches its maximum value at the equilibrium.*

Note that  $S$  is not only defined for isolated systems, but is defined whenever we know the state parameters of a system.

## 4.2 Fundamental thermodynamic identity

Consider an isolated system: its entropy is a function of its internal energy  $U$  and its volume  $V$ . Let us consider the intensive quantity  $\tau$  defined by

$$\frac{1}{\tau} = \left( \frac{\partial S}{\partial U} \right)_V,$$

and consider two systems A and B in contact such that they exchange heat only and they are isolated from the rest of the Universe. The change in the total entropy is

$$dS = dS_A + dS_B = \left( \frac{\partial S_A}{\partial U_A} \right)_V dU_A + \left( \frac{\partial S_B}{\partial U_B} \right)_V dU_B = \left( \frac{1}{\tau_A} - \frac{1}{\tau_B} \right) dU_A, \quad (8)$$

since  $U = U_A + U_B = \text{Constant}$ . The Second Law tells us that when the equilibrium is reached  $dS = 0$ , such that  $\tau_A = \tau_B$ . Moreover, during a transformation we have  $dS > 0$ , such that  $\tau_A > \tau_B$  implies  $dU_A < 0$ : the heat goes from A to B. Therefore  $\tau$  has the characteristics of a temperature and we identify it with  $T$ : we define the entropy such that

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T}. \quad (9)$$

We also define the intensive quantity  $\pi$  by

$$\pi = T \left( \frac{\partial S}{\partial V} \right)_U,$$

and consider that the two systems A and B exchange volume and not heat (their temperature  $T$  is the same), but they are still isolated from the rest of the Universe. Similar arguments as the ones which lead to Eq.(8) give

$$dS = \left( \frac{\pi_A}{T} - \frac{\pi_B}{T} \right) dV_A,$$

since  $V = V_A + V_B = \text{Constant}$ . Again, at the equilibrium  $dS = 0$ , such that  $\pi_A = \pi_B$ . During a transformation we have  $dS > 0$ , such that  $\pi_A > \pi_B$  implies  $dV_A > 0$ : the volume of A increases. Therefore  $\pi$  has the characteristics of a pressure and we identify it with  $P$ : besides the property (9), we also define the entropy such that

$$T \left( \frac{\partial S}{\partial V} \right)_U = P.$$

We conclude that the entropy satisfies the *fundamental* thermodynamic relation, valid in ANY transformation

$$dS = \frac{dU}{T} + \frac{P}{T}dV \quad (\text{any process}). \quad (10)$$

The last relation also implies the important following one: for a reversible process, since  $dU_{rev} = -PdV + \delta Q$ , the infinitesimal change of entropy is

$$dS_{rev} = \frac{\delta Q}{T} \quad (\text{reversible}).$$

Let us see an example where we can make a quantitative identification between  $\tau$  and  $T$ ,  $\pi$  and  $P$ . Consider a gas in a cylinder closed by a piston linked to a spring. The system gas + spring is isolated from the rest of the Universe. The equilibrium of the piston results in the balance of the pressure force due to the gas and the tension of the spring. We have the following parameters: the gas internal energy  $U$ , its entropy  $S$  and its volume  $V$ . The state of the spring is completely determined by the state of the gas since its length is fixed by the volume  $V$  and it has no entropy: the spring is a mechanical system whose state is completely determined by its length (to a macroscopic state corresponds only one microscopic state - see the statistical approach to the notion of entropy in subsection 4.4). The equilibrium state is such that

$$0 = dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = \frac{1}{T}dU + \left(\frac{\partial S}{\partial V}\right)_U dV \quad (11)$$

The global system being isolated, there is no heat exchange and thus  $dU = -PdV$  (we suppose that the small transformations around the equilibrium state are reversible), such that we find from Eq.(11)

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U, \quad (12)$$

which shows the consistency of the previous identifications.

To conclude, let us compute the change in entropy for an ideal gas which goes from the state  $(T_1, V_1)$  to the state  $(T_2, V_2)$ . We have

$$dS = C_V \frac{dT}{T} + nR \frac{dV}{V} = nR \left( \frac{dV}{V} + \frac{1}{\gamma - 1} \frac{dT}{T} \right),$$

such that (we suppose that  $\gamma$  is a constant)

$$S_2 - S_1 = nR \ln \left[ \frac{V_2}{V_1} \left( \frac{T_2}{T_1} \right)^{\frac{1}{\gamma-1}} \right].$$

We note with this result that the entropy increases with the volume and the temperature, which is a general property (for isolated systems).



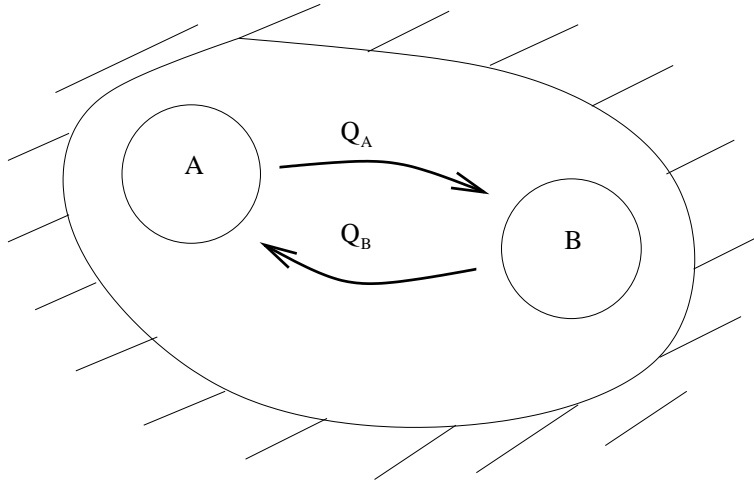


Figure 5: A and B exchange heat only and are isolated from the rest of the Universe. Thus  $Q_A + Q_B = 0$ .

### 4.3 Heat exchanges

Let us see some simple but important examples of computation of change in entropy

Example 1 Two identical systems A and B exchange heat only and are isolated from the rest of the universe (see fig.5). Their initial temperatures are  $T_A$  and  $T_B$  and their heat capacity at constant volume is C.

The equilibrium temperature is  $T_0 = (T_A + T_B)/2$  and we can suppose the transformation reversible since  $S$  is a state function:

$$\Delta S = \int \left( \frac{\delta Q}{T} \right)_A + \int \left( \frac{\delta Q}{T} \right)_B = C \ln \frac{T_0^2}{T_A T_B}, \quad (13)$$

since  $\delta Q = CdT$ . Suppose now that  $T_B/T_A = 1 + \varepsilon$  with  $\varepsilon \ll 1$ . A Taylor expansion of the result (13) gives

$$\Delta S = C \frac{\varepsilon^2}{4} + \dots,$$

such that the entropy is of the *second order* in the difference of temperatures. This result justifies the notion of reversibility: a small step in temperature can in specific cases be considered isentropic.

Example 2 We define a heat reservoir by a system whose temperature does not change, whatever the process occurs in which it exchanges heat with another system. Let  $T_0$  be its

temperature and  $T_1$ ,  $C$  be the initial temperature and heat capacity at constant volume of a system which exchanges heat with the reservoir.

The heat received by the system is  $Q = C(T_0 - T_1)$  such that the change in entropy of the reservoir is  $-Q/T_0 = C(T_1/T_0 - 1)$  since its temperature does not change. The change in entropy of the system is computed in the same way as in the previous example and the total change in entropy is finally

$$\Delta S = C \left( \ln \frac{T_0}{T_1} + \frac{T_1}{T_0} - 1 \right).$$

We can easily check that this result is always positive, showing the irreversibility of the process: an ice cube dropped in the sea will never come back to its initial state.

#### 4.4 Statistical aspect of the entropy

A given isolated system is submitted to a number of constraints, as for example the value of its energy  $U$  and the value of its volume  $V$ . These constraints define a *macroscopic state* of the system. But to each of these macroscopic state corresponds a lot of *microscopic states*. Consider for example a gas in a rigid box which has no interaction with the rest of the universe. A microscopic state would correspond to the list of all the individual positions of the particles, as well as their velocities. Any microscopic state is a priori possible, as long as it is consistent with the given macroscopic constraints of the system.

We say that a microscopic state of a system (in a given macroscopic state) is accessible if this state is consistent with the macroscopic constraints. The starting point in Statistical Physics is to assume that for any isolated system, *each accessible microscopic state has the same probability to occur*.

Let us call  $\Omega$  the number of accessible microscopic states of a system (in a given macroscopic state). The probability of each accessible microscopic state is thus  $1/\Omega$  and we define the statistical entropy  $S_S$  by

$$S_S = k \ln \Omega, \tag{14}$$

where  $k$  is the Boltzmann constant  $k = R/\mathcal{N}$ . This definition helps us understand the idea that the entropy measures the lack of information concerning the microscopic state of the system:  $S_S$  increases with  $\Omega$ .

It is shown that the definition (14) is consistent with all the properties of the thermodynamical entropy  $S$  that we have defined up to now, i.e.  $S_S = S$ . We can check for example the additivity of  $S_S$ : consider a system divided in two parts, with entropies  $S_1 = k \ln \Omega_1$  and  $S_2 = k \ln \Omega_2$ . For each accessible microscopic state of the subsystem 1, we have  $\Omega_2$  accessible microscopic states for the subsystem 2, such that the total number of accessible microscopic states for the global system is  $\Omega = \Omega_1 \Omega_2$ . The global entropy is then

$$S = k \ln \Omega = k \ln (\Omega_1 \Omega_2) = k \ln \Omega_1 + k \ln \Omega_2 = S_1 + S_2,$$

which shows that the statistical entropy is indeed an extensive quantity.

To conclude, we note that the computation of the entropy with its statistical definition is rather an involved task, besides some simple cases as will be seen in section 7.

## 4.5 Third law of Thermodynamics

We have actually defined the *differential*  $dS$  of the entropy with the fundamental relation (10), and not the entropy  $S$  itself. As a consequence, the change in entropy of a system is well defined, but not the value of  $S$  in a given state. We are thus left with an ambiguity which is solved as follows.

Historically, it has been argued that the change in entropy of a system, in any process, vanishes in the limit  $T \rightarrow 0$ . Then, from the statistical interpretation of the entropy in terms of a measure of lack of information concerning the microscopic state of a system, it was assumed by Planck that for a perfect crystal at zero temperature, the entropy is zero. Indeed, the positions of every atom/molecule is exactly known: they are located at the lattice sites of the crystal. As a consequence, the complete microscopic state of the system is known and the entropy should be zero.

The Third Law of Thermodynamics assumes then the following: *the entropy of any system vanishes at zero temperature.*

As a consequence, one can show that the heat capacity of a system should vanish at zero temperature. Indeed, we have

$$dU = TdS - PdV = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - P \right] dV,$$

such that

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V.$$

For a system involved in a transformation at constant volume, we have then

$$S(T_0) = \int_0^{T_0} \frac{C_V}{T} dT,$$

since  $S(0) = 0$  ( $C_V$  should be seen as a  $T$ -dependent function in the previous integral). The only way for this integral to be convergent is to have  $C_V \rightarrow 0$  when  $T \rightarrow 0$ , which proves the property.

## 5 Thermal engines

### 5.1 Carnot-Clausius inequality

We saw in the last section that the entropy  $S$  of a system in contact with a heat reservoir (temperature  $T_0$ ) verifies

$$0 \leq \Delta S_{Total} = \Delta S + \Delta S_{reservoir} = \Delta S - \frac{Q}{T_0},$$

where  $Q$  is the heat taken by the system. We conclude that the change in entropy of the system is such that

$$\Delta S \geq \frac{Q}{T_0}.$$

For a system in contact with  $n$  reservoirs, we have (additivity of the entropy)

$$\Delta S \geq \sum_{i=1}^n \frac{Q_i}{T_i}.$$

In the situation where the system describes cycles, we have  $\Delta S = 0$  such that

$$\sum_{i=1}^n \frac{Q_i}{T_i} \leq 0,$$

which is the Carnot-Clausius inequality, characteristic of the irreversible processes.

As a consequence, let us show that a thermal engine cannot operate with one heat reservoir only: if it was the case, we should have  $Q/T \leq 0$  and thus  $Q \leq 0$ . But the system follows cyclic transformations, such that  $\Delta U = W + Q = 0$ . We conclude that  $W \geq 0$ , which means that the system *takes* work from the surroundings: it cannot be an engine. This property is known as the 'Kelvin statement' of the second law.

Similarly, we have the 'Clausius statement' of the second law: a system which operates in cycles *without work* cannot take heat from a cold reservoir to give it to a hot one. If it was the case (we note  $Q_1 > 0$  the heat taken from the cold reservoir and  $Q_2 < 0$  the heat given to the hot one), we would have  $\Delta U = Q_1 + Q_2 = 0$  and  $Q_1/T_1 + Q_2/T_2 \leq 0$ , what is not possible with  $T_1 < T_2$ .

## 5.2 Carnot's theorem

The general definition of a Carnot cycle is a reversible cyclic process where a system operates between two heat reservoirs.

Let  $T_1$  and  $T_2$  be the two temperatures of the reservoirs ( $T_2 > T_1$  and  $Q_2 > 0$ ,  $Q_1 < 0$ ). The process being reversible, we have for the global system

$$0 = \Delta S_{Total} = \Delta S + \Delta S_{reservoirs} = \Delta S_{reservoirs} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2}.$$

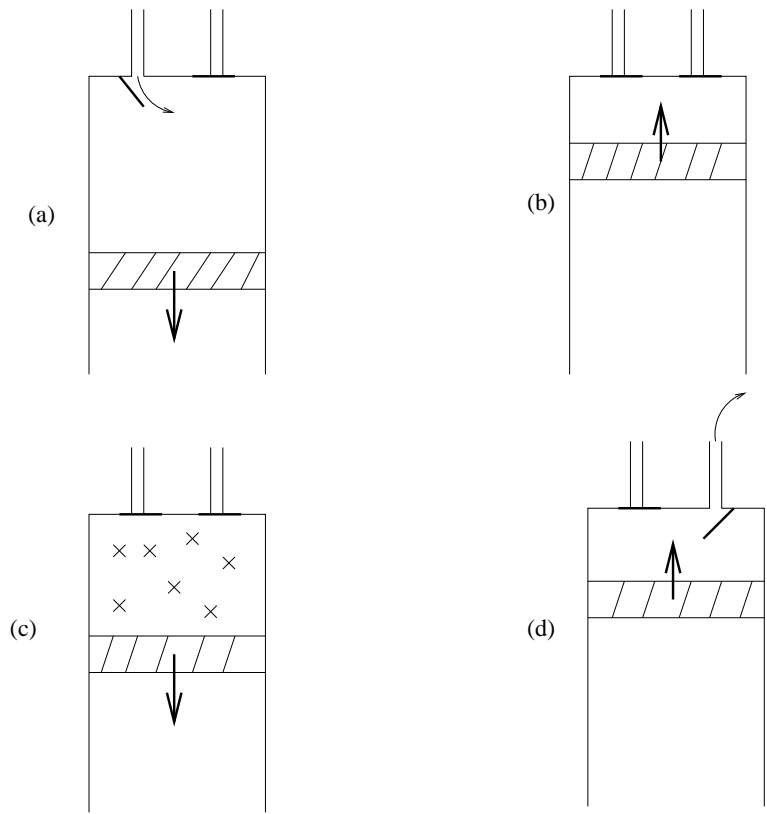


Figure 6: The different phases of a 4-stroke engine. The valves are represented with thick lines. (a) The mixture petrol/oxygen is pumped into the cylinder when the piston goes down. (b) The mixture is compressed as the piston goes up, pushed by the vehicle moving on. (c) The explosion of the mixture pushes the piston down. This is the phase where work is generated by the engine. (d) The piston goes up again and pushes the burned gas outside.

We have seen that the efficiency of the engine is defined as  $\eta = 1 + Q_1/Q_2$  such that

$$\eta_{Carnot} = 1 - \frac{T_1}{T_2},$$

which is the result we found for an ideal gas (in section 3.6). We showed here that it is *independent* of the gas considered and of the details of the transformations (besides reversibility and two isothermic processes). Then, for an irreversible process, since  $\Delta S_{Total} \geq 0$ , we will always have

$$\eta \leq \eta_{Carnot},$$

which is Carnot's theorem.

### 5.3 Refrigerators

A refrigerator *takes* heat from a cold source (the inside of the fridge) to *give* heat to a hot one (the room in which the fridge is) . As we have seen with the Clausius statement of the second law, this is not possible if there is no work. The system that we consider in this case is a fluid which operates in cycles between the two heat reservoirs. A cycle consists in the following steps: the liquid fluid comes inside the fridge, takes heat to evaporate, then is compressed by an electric engine and goes back to the liquid state by giving heat to the outside. The work is the one given by the electric engine which compresses the fluid so as to impose the change of phase gas  $\rightarrow$  liquid and is thus *positive* since it is given to the fluid, whereas it is negative for an engine.

During a cycle, the internal energy does not change, such that  $0 = \Delta U = W + Q_1 + Q_2$ , with  $Q_1 > 0$  and  $Q_2 < 0$ . But  $W > 0$  means that  $Q_1 < |Q_2|$ : the heat taken from the inside is smaller than the heat given to the outside (in absolute value). As a consequence, an open fridge *does not* cool the room in which it is!

## 6 Thermodynamic potentials

### 6.1 Mathematical properties

Implicit functions Let  $f(x, y, z)$  be a function which takes a constant value. We have

$$df = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy + \frac{\partial f}{\partial z} dz = 0. \quad (15)$$

In a plane  $z = \text{Constant}$ ,  $x$  can be seen as an implicit function of  $y$  or  $y$  as an implicit function of  $x$ . We have then from Eq.(15)

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\left(\frac{\partial f}{\partial y}\right)_z}{\left(\frac{\partial f}{\partial x}\right)_z} \quad \text{and} \quad \left(\frac{\partial y}{\partial x}\right)_z = -\frac{\left(\frac{\partial f}{\partial x}\right)_z}{\left(\frac{\partial f}{\partial y}\right)_z},$$

such that

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1.$$

This can be checked for example with the equation of state of an ideal gas:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2} = \left(\frac{\partial V}{\partial P}\right)_T^{-1}.$$

We can also easily check that

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

Legendre transform Let  $f(x)$  be a function and call its derivative  $y = f'(x)$ .  $y$  is a function of  $x$  but we suppose that the relation can be inverted such that we consider  $x$  as a function of  $y$ . Define then  $g = f - xy$ . The derivative of  $g$  with respect to  $y$  is

$$\frac{dg}{dy} = \frac{df}{dx} \frac{dx}{dy} - x - \frac{dx}{dy}y = -x.$$

We see that  $g$  has natural variable  $y$  since its derivative is known and simple.  $g$  is called the Legendre transform of  $f$ . Another interesting property of the Legendre transform deals with its second derivative:

$$\frac{d^2g}{dy^2} = -\frac{dx}{dy} = -\left(\frac{dy}{dx}\right)^{-1}, \quad (16)$$

such that we have the simple relation between the second derivatives of  $f$  and  $g$ :

$$g''(y) = -[f''(x)]^{-1}. \quad (17)$$

As an example, we have  $H = U + PV$ , such that the enthalpy  $H$  is the Legendre transform of the internal energy  $U$  with respect to the variable  $-V$  ( $S$ , the other variable of  $U$ , does not play a role here). Therefore we have  $(\partial H/\partial P)_S = V$ .

## 6.2 Helmholtz and Gibbs free energies

$S$  and  $V$  are the natural variables of  $U$ . But these variables might not be convenient from the experimental point of view. Suppose that the convenient variables are  $T$  and  $V$ . We define then the *Helmholtz free energy*  $F$  as the Legendre transform of the internal energy with respect to the variable  $S$

$$F(T, V) = U(S, V) - TS,$$

such that  $dF = -SdT - PdV$  and thus

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{and} \quad \left(\frac{\partial F}{\partial T}\right)_V = -S.$$

On the other side, if we know the variables  $T$  and  $P$ , it is convenient to define the *Gibbs free energy*  $G$  as the Legendre transform of the enthalpy with respect to the variable  $S$

$$G(T, P) = H(S, P) - TS,$$

such that  $dG = -SdT + VdP$  and thus

$$\left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S.$$

Note that  $G$  is a Legendre transform of  $U$  with respect to both variables  $S$  and  $-V$ :  $G(T, P) = U(S, V) + PV - TS$ . Of course,  $H$ ,  $G$  and  $F$  are state functions as  $U$  and  $S$ .

Finally, note that these functions contain all the same physics. If we know one of them, we can find the others. The Legendre transform just involves a change of variables which are more convenient for a given physical problem.

Why do we introduce  $F$  and  $G$ ? Consider a system depending also on other parameters that  $P$ ,  $V$  or  $T$  and which transforms under a process where  $T$  and  $V$  are constant. This system can exchange heat with the surroundings. In this situation, we have seen that  $\Delta U = Q$  and  $\Delta S \geq Q/T$ , so that the evolution of the system is such that  $\Delta F \leq 0$ . If now the system transforms under a process where  $T$  and  $P$  are constant, we have  $\Delta H = Q$  and  $\Delta S \geq Q/T$  so that this time the evolution of the system is such that  $\Delta G \leq 0$ .

We could consider  $U$  as a function of  $(T, V)$  or  $(T, P)$ , but the evolution of the system would not be ruled by simple conditions on  $U$  as we have for  $F$  or  $G$ .

## 6.3 Maxwell relations

A function  $f$  of two variables  $x$  and  $y$  is such that its derivatives with respect to  $x$  and  $y$  commute. Hence



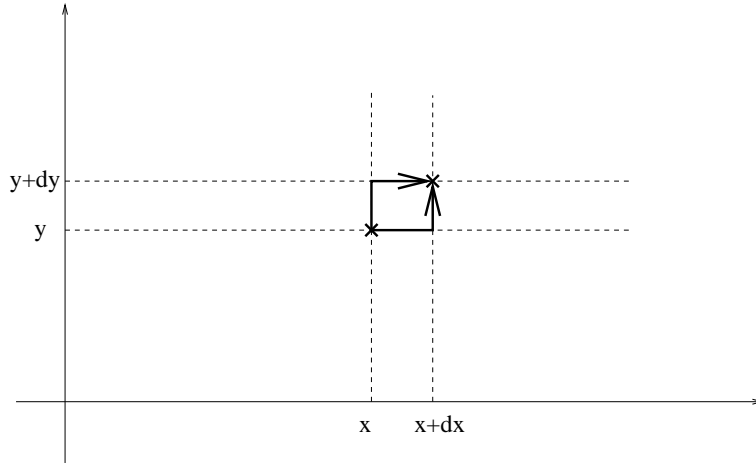


Figure 7: Commutativity of the partial derivatives. A derivative with respect to a variable tells how the function changes when this variable increases by an infinitesimal quantity. Going from  $(x, y)$  to  $(x+dx, y+dy)$  can be done in two different ways:  $(x, y) \rightarrow (x+dx, y) \rightarrow (x+dx, y+dy)$  and  $(x, y) \rightarrow (x, y+dy) \rightarrow (x+dx, y+dy)$ . Both ways lead to the same result.

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}. \quad (18)$$

If we apply this property to the different state functions that we introduced, we obtain:

$$\begin{aligned} dU &= TdS - PdV \quad \text{such that} \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \\ dF &= -SdT - PdV \quad \text{such that} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \\ dH &= TdS + VdP \quad \text{such that} \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \\ dG &= -SdT + VdP \quad \text{such that} \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \end{aligned}$$

## 6.4 Energy equation

Let us consider a system with independent variables  $T$  and  $V$ . We have

$$TdS = dU + PdV = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT,$$

such that

$$T \left( \frac{\partial S}{\partial V} \right)_T = P + \left( \frac{\partial U}{\partial V} \right)_T,$$

and with the Maxwell relation obtained from  $dF$ , we finally have

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P. \quad (19)$$

This equation tells us that for an ideal gas,  $(\partial U/\partial V)_T = 0$ : *the internal energy depends on the temperature only*. We thus generalized to any ideal gas this result which was derived with a microscopic model in the case of the monoatomic ideal gas. Besides, the present derivation is independent of any microscopic consideration.

## 6.5 Generalized Mayer relation

The relation (5) was valid for ideal gas only and we can generalize it to any fluid depending on two independent parameters. If we look at the internal energy as a function of  $T$  and  $V$ , we define

$$dU = C_V dT + (l - P) dV, \quad (20)$$

where  $C_V$  and  $l$  are parameters which in general depend on  $T$  and  $V$ . Note that in the case of an ideal gas  $l_{ideal} = P$  since  $U$  depends on  $T$  only. From the definition (20), we have  $l = (\partial U/\partial V)_T + P$  and with the energy equation, we find then

$$l = T \left( \frac{\partial P}{\partial T} \right)_V. \quad (21)$$

Note here that with this relation, it is easy to check that  $l_{ideal} = P$ . The heat capacity  $C_P$  appears in the enthalpy. We have

$$dH = d(U + PV) = \left[ C_V + l \left( \frac{\partial V}{\partial T} \right)_P \right] dT + \left[ V + l \left( \frac{\partial V}{\partial P} \right)_T \right] dP,$$

so that

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = C_V + l \left( \frac{\partial V}{\partial T} \right)_P,$$

and finally, using Eq.(21)

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P.$$

One can easily check this generalized Mayer relation in the case of an ideal gas. Remember that in the general case,  $C_P$  and  $C_V$  do not depend on  $T$  only (as it is the case for an ideal gas) but are functions of two independent variables.

## 7 Other systems

### 7.1 Van der Waals gas

So far we have seen one example of equation of state, for the ideal gas. The Van der Waals equation of state takes into account non ideal effects corrections. It reads, for one mole

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT. \quad (22)$$

In Eq.(22), the parameter  $b$  corresponds to the volume (small compared to  $V$ ) occupied by the particles of the gas which actually have a finite size and they cannot interpenetrate. The term  $a/V^2$  (small compared to  $P$ ) corresponds to a dynamical pressure due to the interaction between particles. For  $n$  moles, we have to make the substitutions  $a \rightarrow n^2a$ ,  $b \rightarrow nb$  and  $R \rightarrow nR$ , since  $P$  and  $T$  are intensive variables and  $V$  is extensive.

Let us study one effect of this equation of state: the volume dependence of the internal energy. Write

$$dU = C_V dT + (l - P)dV, \quad (23)$$

and suppose that the real gas expands freely from the volume  $V_1$  to the volume  $V_2 > V_1$  in an adiabatic process, such that  $dU = 0$  since there is no heat or work exchanged with the surroundings. For an ideal gas, this should imply that  $dT = 0$  but for a real gas, this implies a temperature change. We have from Eq.(23) and  $dU = 0$

$$\frac{dT}{dV} = \frac{P - l}{C_V} = -\frac{a}{C_V V^2}, \quad (24)$$

since we obtain from the equation of state (22)

$$P = \frac{RT}{V - b} - \frac{a}{V^2},$$

and we know that (see Eq.(21))

$$l = T \left( \frac{\partial P}{\partial T} \right)_V = \frac{RT}{V - b}.$$

Let us show that in the case of Van der Waals gas, the heat capacity  $C_V$  does not depend on the volume: the expression of  $dU$  implies (see property (18))

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}(l - P)\right)_V = \left(\frac{\partial}{\partial T}\left(\frac{a}{V^2}\right)\right)_V = 0, \quad (25)$$

such that  $C_V$  depends on  $T$  only. The general principles of Thermal Physics give us the property (25) but cannot lead to the knowledge of  $C_V$  itself: we need to develop microscopic models if we wish to find the temperature dependence of  $C_V$ . But the change in temperature being small for the process under study, we will suppose that  $C_V$  is a constant. We have then from Eq.(24)

$$\Delta T = \int_{V_1}^{V_2} dT = \frac{a}{C_V} \left(\frac{1}{V_2} - \frac{1}{V_1}\right) < 0.$$

A Van der Waals gas does not follow the first Joule law and cools down in a free expansion.

## 7.2 Stretched wire

We will briefly describe here the similarities between the study of a stretched wire and the study of a gas.

The length of a wire depends on the force  $f$  acting on it and on the temperature  $T$ . The work  $\delta W$  necessary to generate the extension  $dx$  of the wire is  $\delta W = +fdx$ . The infinitesimal change in the internal energy is then

$$dU = TdS + fdx,$$

where  $S$  is the entropy of the wire. The differential of the free energy  $F$  is

$$dF = -SdT + fdx,$$

such that the corresponding Maxwell relation reads

$$\left(\frac{\partial f}{\partial T}\right)_x = -\left(\frac{\partial S}{\partial x}\right)_T. \quad (26)$$

If we now wish to consider  $U$  as function of  $T$  and  $x$ , we introduce the heat capacity at constant length  $C_x$  and the parameter  $k$  (which are functions of  $T$  and  $x$ ) to parametrize  $dU$  as follows

$$dU = C_x dT + (k + f)dx.$$

But we also have

$$dU = T \left( \frac{\partial S}{\partial T} \right)_x dT + \left[ T \left( \frac{\partial S}{\partial x} \right)_T + f \right] dx,$$

such that, taking into account the Maxwell relation (26), we obtain

$$k = -T \left( \frac{\partial f}{\partial T} \right)_x.$$

This system is thus very similar to a gas, where  $-f$  plays the role of the pressure and  $x$  plays the role of the volume. The equation of state can be for example given by the law  $x = x(f, T)$ , which of course depends on the wire.

### 7.3 Black body radiation

Consider a cavity of volume  $V$  with walls at temperature  $T$ , generating an electromagnetic radiation inside the cavity. A black body is such a cavity which re-emits all the radiation absorbed by its walls. The electromagnetic waves induce a radiation pressure  $P$  on the walls of the cavity and we can consider this system as a gas of photons, with state variables  $(P, V, T)$ .

Our aim is to derive the so called Stefan's Law giving the temperature dependence of the energy radiated by a black body.

For this, we write the internal energy of the cavity radiation as  $U = Vu(T)$ , since it is an extensive quantity. To find the radiation pressure, we use the kinetic pressure (3) that we derived for an ideal gas:

$$P = \frac{mN}{3V} c^2 = \frac{1}{3} \rho c^2,$$

where  $c$  is the speed of light and  $\rho$  the "mass density" of photons. From the relativistic mass/energy relation we know that  $\rho = u/c^2$ , such that

$$P = \frac{1}{3} u.$$

We have now all the required state variables and can use the energy equation (19) which reads then

$$u = \frac{T}{3} u' - \frac{1}{3} u,$$

where  $u'$  is the derivative of  $u$  with respect to  $T$ . The integration of this equation leads to

$$u(T) = \text{Constant} \times T^4,$$

which is Stefan's law. Note that to derive this result we needed a microscopic assumption: we supposed that the light is composed of particles, which is a quantic property. We could not have derived Stefan's law with the general principles of thermodynamics only.

## 7.4 Spin temperature

We will consider a simple example where the statistical entropy of a system can be computed: the perfect paramagnetic crystal. We will then compute the temperature of this system of spins.

Consider  $N$  spins on the nodes of a crystal, in a magnetic field  $\vec{B}$ . To each spin  $\vec{S}$  can be associated a magnetic moment  $\vec{\mu} = \gamma\vec{S}$  whose component along  $\vec{B}$  can take two values  $\pm\mu_0$ . We will neglect the interactions between the spins and consider only their coupling to the external field  $\vec{B}$ . The energy of a spin is then  $\pm\mu_0 B$  and the total energy is  $E = (n^- - n^+)\mu_0 B$ , where  $n^-$  and  $n^+$  are the numbers of spin down and up respectively. These numbers also satisfy  $n^- + n^+ = N$ , such that

$$n^- = \frac{1}{2} \left( N + \frac{E}{\mu_0 B} \right) \quad \text{and} \quad n^+ = \frac{1}{2} \left( N - \frac{E}{\mu_0 B} \right).$$

The number of accessible microscopic states for a given macroscopic state is

$$\Omega = \frac{N!}{n^-!n^+!},$$

such that the entropy is

$$S = k \ln \Omega = k \ln N! - k \ln \left( \frac{N}{2} + \frac{E}{2\mu_0 B} \right)! - k \ln \left( \frac{N}{2} - \frac{E}{2\mu_0 B} \right)!$$

The Stirling approximation

$$\ln N! \simeq N \ln N - N \quad \text{for large } N$$

can be used if we suppose that  $n^-$  and  $n^+$  are of the order of  $N/2$  and gives

$$\begin{aligned} S_S \simeq kN \ln N & - k \left( \frac{N}{2} + \frac{E}{2\mu_0 B} \right) \ln \left( \frac{N}{2} + \frac{E}{2\mu_0 B} \right) \\ & - k \left( \frac{N}{2} - \frac{E}{2\mu_0 B} \right) \ln \left( \frac{N}{2} - \frac{E}{2\mu_0 B} \right). \end{aligned}$$

We can now compute the temperature of the system and find that

$$\frac{1}{T} = \frac{\partial S_S}{\partial E} \simeq \frac{k}{2\mu_0 B} \ln \left( \frac{N - E/\mu_0 B}{N + E/\mu_0 B} \right). \quad (27)$$

Note that  $T$  given by Eq.(27) can be *negative*, depending on the sign of  $n^- - n^+$ , that is on the sign of  $E$ ! This comes from the fact that in a system with a *finite* number of degrees of freedom, the entropy can be a decreasing function of the energy. But we must not forget that the model considered here excludes any other interaction than the coupling to the external field. It is never the case in reality and this negative temperature situation is accessible only during a relaxation time, *out of equilibrium*, where in principle we cannot define the temperature and where the other interactions neglected here have not led to an equilibrium state yet.

## 8 Changes of phase

### 8.1 Chemical potential

For the study of phase transitions, the Gibbs free energy  $G$  is very useful, since we usually know  $T$  or  $P$ . Consider an equilibrium between the liquid ( $n$  moles) and vapour ( $n'$  moles) phases of a given constituent, together in a closed box. Both individual systems are *open* since they can exchange matter: their number of moles is not constant. We define then the chemical potential  $\mu$  of the liquid and  $\mu'$  of the vapour by

$$\begin{aligned} dG_{liquid} &= -SdT + VdP + \mu dn \\ dG_{vapour} &= -S'dT + V'dP + \mu' dn' \end{aligned}$$

If we let the system evolve from an out-of-equilibrium state, we know that the evolution is such that  $dG = dG_{liquid} + dG_{vapour} \leq 0$ . At constant pressure and constant temperature, we have then  $(\mu - \mu')dn \leq 0$  since  $n + n' = \text{Constant}$ . Therefore  $dn > 0$  implies  $\mu' > \mu$ : the matter transforms from the phase with the *larger* chemical potential towards the phase with the *smaller* chemical potential. At the equilibrium state,  $dG = 0$  since  $G$  reaches its minimum (the entropy reaches its maximum) and the chemical potentials are thus equal:

$$\mu = \mu' \quad (\text{equilibrium}).$$

These results are general and concern also the chemical reactions where we usually have more than 2 open systems.

The Gibbs free energy  $G$  can be expressed in terms of the chemical potentials of the different constituents that are present in a given phase. With  $c$  constituents,  $G$  is a function of  $T$ ,  $P$  and  $n_1, n_2, \dots, n_c$ .  $G$  being an extensive function, it has the following property:

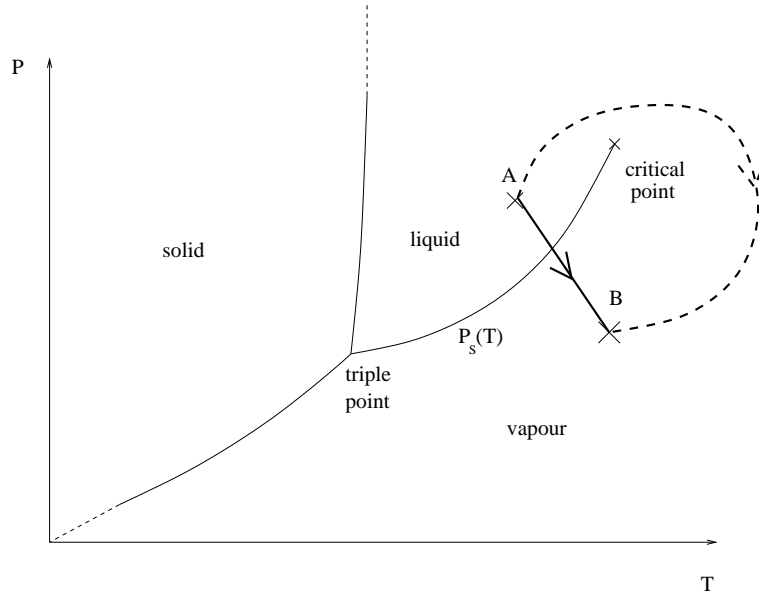


Figure 8: Three phases in the diagram  $(P, T)$ . The lines represent states where two phases are in contact. At the triple point, the three phases are in contact. Liquid and gas are not fundamentally different: a process from  $A$  to  $B$  involves a phase transition along the continuous path, whereas no phase transition occurs along the dashed path which goes around the critical point. The curve joining the triple point and the critical point is the saturated vapour pressure  $P_S(T)$ .

$$G(T, P, \lambda n_1, \dots, \lambda n_c) = \lambda G(T, P, n_1, \dots, n_c),$$

for any  $\lambda$ . A derivative with respect to  $\lambda$  leads then to the general property

$$G = \sum_{i=1}^c \mu_i n_i, \quad (28)$$

since  $\mu_i = \partial G / \partial n_i$ .

The chemical potential is an intensive variable and thus depends on intensive quantities only:  $T$ ,  $P$  and the molar fractions  $x_i = n_i / (n_1 + \dots + n_c)$ .

## 8.2 Phase rule

Suppose that we have  $c$  constituents in  $\phi$  phases, in equilibrium under fixed  $T$  and  $P$ . We have then  $c\phi + 2$  parameters: the molar fraction  $x_i$  of each constituent in each phase, the temperature and the pressure. But these parameters are not independent: the sum of the molar fractions gives 1 in each phase ( $\phi$  relations) and the equilibrium implies the equality



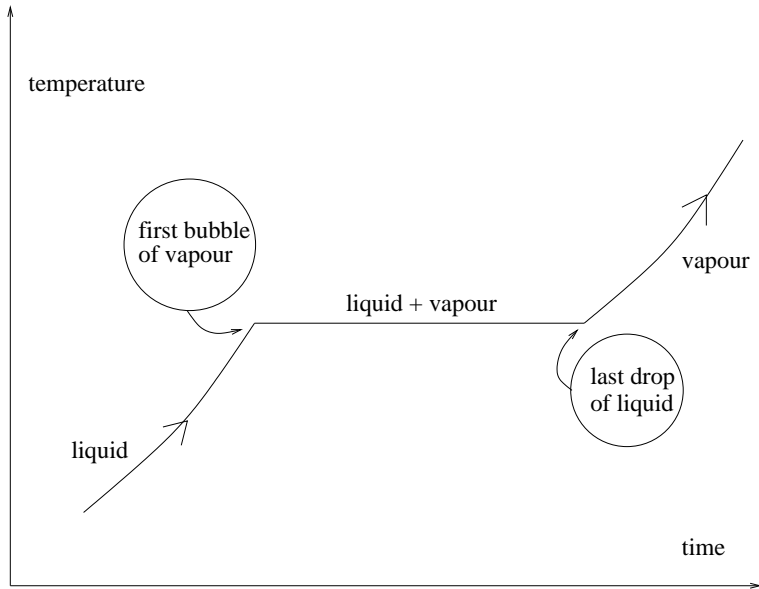


Figure 9: A liquid is heated up at **constant pressure**: when the first bubble of vapour appears, the two phases are in contact and the temperature follows a plateau until the last drop of liquid disappears.

of the chemical potentials for the  $c$  constituents in each phase ( $c\phi - 1$  relations). The number of independent parameters is then

$$n = c\phi + 2 - [\phi + c(\phi - 1)] = c + 2 - \phi.$$

For a pure constituent in equilibrium between two phases, we have then 1 independent parameter. Thus the pressure  $P$  is a function of the temperature  $T$  (or the opposite), such that  $T$  is constant during a phase transition at a given pressure.

If a pure constituent is in equilibrium between three phases, the phase rule tells us that there are *no* free parameters anymore. Thus the triple point exists only for *one* set of parameters  $T, P$ . For water, we have  $T_{triple} = 273.16$  K and  $P_{triple} = 597.27$  Pa (approximately 0.6 per cent of an atmosphere).

### 8.3 Evaporation

Consider a box with a given volume  $V$ , containing the liquid and the vapour phases of a given constituent ( $N$  moles in total). The phases are in equilibrium at the temperature  $T$  (we neglect the volume of the liquid phase compared to the volume of the vapour). Since we have one free parameter (say  $T$ ), the pressure is given by a function  $P_S(T)$ , called the *saturated vapour pressure*. If we consider the vapour as an ideal gas, it verifies

$$P_S(T)V = n(T)RT,$$

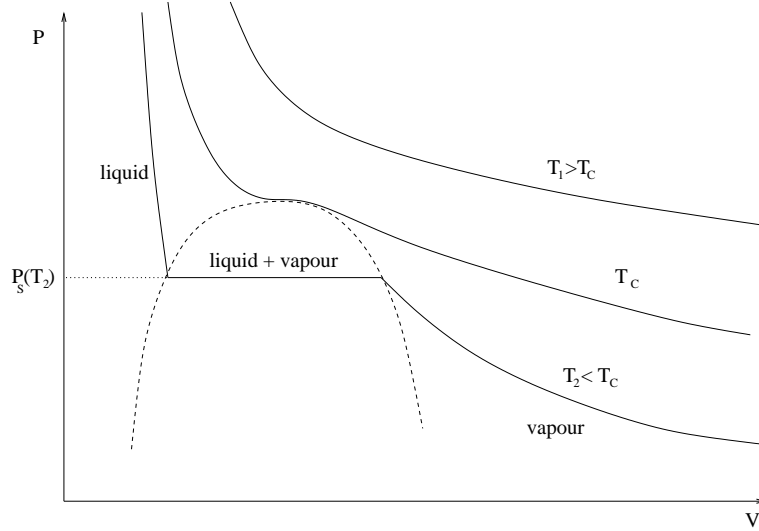


Figure 10: If the volume of a liquid increases at **constant temperature**: (i) For a temperature lower than the critical temperature  $T_C$ , when the first bubble of vapour appears, the two phases are in contact and the pressure follows a plateau until the last drop of liquid disappears. (ii) For a temperature larger than  $T_C$ , there is no distinction between liquid and vapour.

where the number of moles  $n(T)$  is *not* constant, since liquid is evaporating: both vapour and liquid are open systems. Thus  $P_s$  is not a linear function of  $T$ , it is actually growing up quicker and its precise evolution with  $T$  depends on the constituent under study. When the temperature increases and the last drop of liquid disappears, the vapour contains all the matter (constant number of moles) and we recover the usual ideal gas equation of state: the pressure grows linearly with the temperature.

The *latent heat*  $L$  is the heat necessary for the unit mass to change of phase, at a given temperature. We know that the transition occurs at fixed temperature and pressure, such that  $L = \Delta h = \Delta g + T\Delta s$ , where  $\Delta h, \Delta g, \Delta s$  are the differences, per unit mass, of the enthalpy, the Gibbs free energy and the entropy respectively, between the two phases. The Gibbs free energy in the whole process of the phase transition does not change since the temperature and the pressure remain the same and the chemical potentials are equal, such that  $L = T\Delta s$ . The latent heat can then be linked to the slope  $dP_s/dT$  as follows. The equilibrium is such that  $\mu_1 = \mu_2$  (the indices 1 and 2 denote the phases) and the derivative of this equality with respect to the temperature gives

$$\left(\frac{\partial\mu_1}{\partial T}\right)_P + \left(\frac{\partial\mu_1}{\partial P}\right)_T \frac{dP_s}{dT} = \left(\frac{\partial\mu_2}{\partial T}\right)_P + \left(\frac{\partial\mu_2}{\partial P}\right)_T \frac{dP_s}{dT}. \quad (29)$$

The chemical potentials are Gibbs free energies per unit mass (see Eq.(28)) and thus we have

$$\left(\frac{\partial\mu}{\partial P}\right)_T = v \quad \text{and} \quad \left(\frac{\partial\mu}{\partial T}\right)_P = -s,$$

where  $v$  and  $s$  are the volume and entropy per unit mass respectively. Eq.(29) gives then

$$\frac{dP_s}{dT}(v_2 - v_1) = s_2 - s_1,$$

and the latent heat is finally given by

$$L = T\Delta v \frac{dP_s}{dT}. \quad (30)$$

This last equation is the Clausius-Clapeyron equation and gives the latent heat to go from the phase 1 to the phase 2 with  $\Delta v = v_2 - v_1$ . Note: if the latent heat is defined per unit mole,  $\Delta v$  is the difference of volume per unit mole.

## 8.4 Orders of phase transitions

**First Order:** In the example of the change of phase (liquid  $\longleftrightarrow$  vapour), two phases coincide and each of these phases has its own volume per unit mass  $v$  and entropy per unit mass  $s$ . As a consequence, there is a discontinuity in the first derivatives of the Gibbs free energy per unit mass  $g$  since  $dg = -sdT + vdP$ .

In general, a first order phase transitions is such that the first derivatives of the Gibbs free energy are discontinuous (the Gibbs free energy itself is continuous). In these transitions, due to the discontinuity of the volume per unit mass, there is a latent heat given by the Clausius-Clapeyron equation (30).

*Examples:*

- (liquid  $\longleftrightarrow$  vapour) and (solid  $\longleftrightarrow$  liquid);
- (superconducting  $\longleftrightarrow$  normal metal) with an external magnetic field applied to the sample.

**Second Order:** In this case, the first derivatives of the Gibbs free energy are continuous, but not the second derivatives. A physical quantity that is discontinuous is for example the heat capacity per unit mass. To see this, consider the enthalpy per unit mass  $h$ , with differential

$$dh = Tds + vdP = T \left(\frac{\partial s}{\partial T}\right)_P + \left[ v + T \left(\frac{\partial s}{\partial P}\right)_T \right] dP.$$

The heat capacity at constant pressure is then, per unit mass,

$$c_p = \left( \frac{\partial h}{\partial T} \right)_P = T \left( \frac{\partial s}{\partial T} \right)_P = -T \left( \frac{\partial^2 g}{\partial T^2} \right)_P,$$

and is discontinuous as a second derivative of  $g$ .

*Examples:*

- (superconducting  $\longleftrightarrow$  normal metal) without external magnetic field;
- (superfluid  ${}^4\text{He}$   $\longleftrightarrow$  normal liquid  ${}^4\text{He}$ );
- (ferromagnetic  $\longleftrightarrow$  paramagnetic).