(Basic) Thermodynamics

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September 20, 2021

1 Introduction

Thermodynamics traditionally studies the features of a system made of an extremely large number N of molecules. Typical systems involve a large number n of moles of a substance, where $N = n \cdot N_A$, with $N_A = 6.022 \cdot 10^{23}$ mol^{-1} being Avogadro's constant. To get a feeling for numbers, a liter of water at room temperature contains roughly 56 moles, which means that in a 1 l bottle one finds as many as $3.4 \cdot 10^{25}$ water molecules. This gargantuan number makes it impossible to study a thermodynamic system with the standard approach provided by integration of the laws of Newton for all the particles in the system. One is usually interested only in certain global features, so that it is not always necessary to know precisely the microscopic details, although it is always a good idea to have a feeling of what is happening also at the microscale. One of the main variables determining the behavior of a system is its *temperature* T. It is beyond the scope of these notes to dive into the precise definition of temperature. For our purposes, we here define it as that quantity that is the same for two systems that can exchange heat with each other and are at equilibrium.

2 Laws of thermodynamics

The main pillars of thermodynamics are four laws which, albeit generic, enable the development of a very powerful theoretical framework, which is capable of describing the many fancy properties displayed by real systems in the whole temperature range accessible to experiments. Before going into their definition, it is useful to spend some words on the concept of *equilibrium*. Two systems in contact can exchange energy and/or matter with each other. Hence, one can think that there is a certain flow going from system A to system B, and another flow going from B to A. When the two systems are at equilibrium, the two flows are equal in magnitude, so that the *net* flow is zero. In other terms, the systems are still exchanging energy and/or matter, but the two flows compensate each other. There are in practice three equilibria to consider:

- *Thermal equilibrium.* In this case, one is considering the flow of energy by means of heat exchange. The physical quantity accounting for thermal equilibrium is the *temperature*.

- *Mechanical equilibrium.* Here, the flow of energy is obtained by means of mechanical work of a system onto the other. When there is mechanical equilibrium, the two systems have the same *pressure*.

- *Chemical equilibrium.* This refers to the flow of particles between systems that can exchange matter. The two systems are at chemical equilibrium if they have the same *chemical potential*.

2.1 Zeroth law

The zeroth law of thermodynamics assumes that the equilibrium has the transitive property. Therefore, if system A and C are both in equilibrium with system B, then they are also in equilibrium with each other. Note that the very definition of equilibrium stated above is implicity assuming the validity of this law.

2.2 First law

The first law of thermodynamics states the conservation of energy. In classical mechanics, in absence of friction the energy E is computed as the sum of the potential and the kinetic energy, and is a conserved quantity. Within the present context, we refer to it as the *internal energy* of the system. When friction is present, E is not conserved anymore, due to the dissipation induced by the friction. Nevertheless, conservation of energy is not violated: the missing part has been pumped into the body with which the system of interest is making friction, although in a disordered way. Our system has exchanged a certain amount of *heat* ΔQ with the frictioning body. Here, we employ the convention according to which $\Delta Q < 0$ if the heat is flowing away from the system (as in this case), while $\Delta Q > 0$ if it is pumped into the system. In the case that we are analyzing, conservation of energy can be thus stated as $\Delta E = \Delta Q$, where ΔE is

the change in internal energy. There is also a second channel through which energy can be exchanged, namely by doing a work ΔW. We consider here the convention according to which $\Delta W < 0$ if the work is performed by the system (for instance if a gas is expanding), while $\Delta W > 0$ is the work is performed onto the system (e.g. if the gas is compressed). The first law of thermodynamics is thus stated as:

$$\Delta E = \Delta Q + \Delta W \; . \tag{1}$$

One can think of this law in terms of a monetary analogy. In the analogy, E is the amount of money that one owns. Heat and work are two possible ways in which money can be exchanged with others (e.g. cash or bank transfer). In the present convention, we always consider an exchange of money as positive if it is incoming and negative if it is outgoing. Within this analogy, Eq. (1) simply computes the changes in the total amount present on the bank account after some exchange of money. Important note: different sources use different sign conventions, so when employing formulas it is important to have a clear idea of which convention is being used!

For completeness, we also mention that the internal energy of a system can also change due to a variation in the number of particles that compose it. For instance, if one temporarily opens a valve in a box full of gas the total number of molecules will change. The *chemical potential* μ can be defined as the amount of internal energy "stored" in one molecule, so that the first law in this case reads

$$\Delta E = \Delta Q + \Delta W + \mu \Delta N, \tag{2}$$

where ΔN is the change in the number of molecules. If there are different kinds of molecules in the system, each of them will have in general a different associated chemical potential μ_i, so that the first law has to be modified accordingly.

2.3 Second law

The first law allows any thermodynamic transformation that complies with Eq. (1). Particularly, for a thermodynamic cycle (where the starting and final state are the same), one has $\Delta E = 0$, so that as a net result $\Delta W = -\Delta Q$. Naively, one could then imagine to consider a cycle working only with a certain external source from which to drain some heat ($\Delta Q > 0$). In this way, one would obtain the integral transformation of heat (a disordered form of energy) into a work $\Delta W < 0$ performed by the system (an ordered form of energy, which can be used to power machines). As it turns out, this is too optimistic, and there are some theoretical boundaries that are set by the second law of thermodynamics. Particularly, according to the *Clausius formulation of the second law of thermodynamics, it is impossible to realize a thermodynamic process whose only outcome is the transfer of heat from a cold source at temperature T_{cold} into a hot source $T_{hot} > T_{cold}$.* This law is intimately connected to the concept of irreversibility and entropy, as we will see below.

2.4 Third law

The third law of thermodynamics states that it is impossible to reach $T = 0$ in a finite number of reversible thermodynamic transformations. As in the case of the second law, the quantitative formulation of the third law involves entropy, stating that when $T \to 0$ the changes in entropy of any reversible transformation tend to zero, which in practice prevents the possibility of reaching the absolute zero in real systems.

3   State variables

State variables are used to characterize the state of a system. For instance, in order to characterize the air in a room, one needs to determine e.g. its density, volume, temperature and pressure. By construction, they depend only on the state of the system and not on its history. Therefore, when performing a thermodynamic transformation from state A to state B, in order to determine the state variables it does not matter which transformation we are performing, but only the states involved. While this is evident for variables such as temperature or pressure (by definition, if the system is prepared in a state with temperature T, its temperature will be equal to T independently of how we reach it), it becomes less trivial for other quantities, e.g. entropy or the internal energy. Even more importantly, there are some other quantities which *do* depend on the particular transformation performed, namely heat and work. These *do not* define state variables, as they are not univoquely determined by the initial and final states. As a consequence, one can not speak of heat or work "of a system", but rather heat "exchanged" by a system or work "performed" by (or onto) a system. As one can notice, the words used imply an inherent change of the system underlying heat or work, i.e. they are directly related not only to the initial and final states, but also to the particular transformation employed (although they are related to state variables, as will be discussed later). This discussion will become clearer below, when we treat some examples.

At a general level, state variables are divided into two classes, namely extensive and intensive quantities. *Extensive quantities* are those variables whose value scales with the amount of matter in the system. For instance, the number of molecules N is an extensive quantity, as it scales proportionally to the amount of matter (as a matter of fact, N defines the amount of matter, so this is a tautology!). Also the volume V is an extensive quantity, provided that the system is kept at the same conditions: in order to contain $2 \cdot N$ molecules, one needs a room twice as big. In contrast, for *intensive quantities* the value is independent of the size of the system. For instance, the density ρ does not depend on whether we have N or $2 \cdot N$ molecules, provided that the volume of the room is scaled accordingly. Other key intensive thermodynamic quantities are the pressure p and the temperature T. Note that one can easily obtain an intensive quantity starting from an extensive one and dividing by N. For instance, the total mass of air in the room, M, is an extensive quantity. However, $m = M/N$ is an intensive quantity and corresponds to the mass of a molecule of air.

Problem. In order to make a collection of N *jamones* age, a physicist decides to store them in a room and let them hang from the ceiling by hooking each of them to a different spring. All the springs have the same elastic constant k, the mass of a jamón is m and the gravitational acceleration is g. What is the total elastic energy stored in the collection of springs? Is it an extensive or an intensive quantity (with respect to N)?

Problem. A group of N physicists want to push a huge box of dimensions $w \times w \times h$, where h is the height. They align in front of one side of the box and start pushing at the same time, each of them applying a force with magnitude f and perpendicular to a lateral face of the box (with dimensions $w \times h$). Is the force f an extensive or an intensive quantity? What about

the total force applied? Compute the pressure exerted by the physicists (remember that the pressure is computed as the ratio between the applied force and the extension of the surface on which it is applied). Is it extensive or intensive (assume that the width of the box scales with the number of physicists, so that their spacing is constant)? After a lot of effort, the physicists manage to displace the box by a length l. What is the work performed by our heroes (remember that work is the product between force and displacement, assuming that they are oriented in the same direction)? Is is extensive or intensive? For each of the extensive quantities of this problem, build the corresponding intensive quantity and think of its physical interpretation.

4 Open, closed and isolated systems

As mentioned above, *state variables* are the physical quantities characterizing a thermodynamic system. The thermodynamic state can be modified by letting some exchange of energy or matter with the surrounding medium. Particularly, there are three main routes in which this is achieved: i) exchange of particles; ii) exchange of heat; iii) work performed by or onto the system.
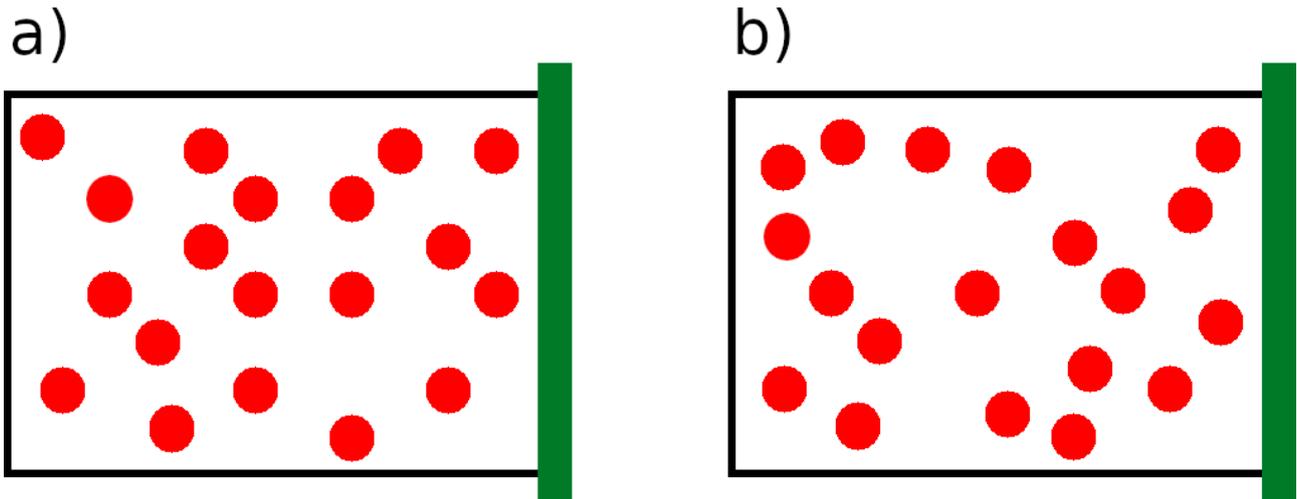

Figure 1: A box containing N particles at a certain density ρ and at a temperature T.

In Fig.1a, we consider a box containing N particles with a density ρ and at temperature T. We assume that no exchange of matter with the outside is possible (i.e. there are no holes); analogously, there is no flux of energy (either in the form of work or heat exchange). This prevents any form of "communication" between the inside and the outside, so that the system keeps its thermodynamic state. Hence, the state variables of the system do not change in time. However, this is true only for the thermodynamic state, which looks at the system from a macroscopic perspective. Microscopically, there is a constant movement of particles inside the box, which interact with each other and with the wall. Particularly, in the simplest case of an *ideal gas*, they do not interact with each other and just bounce elastically on the wall (i.e. the velocity of a bouncing particle does not change in magnitude; if this was not the case, there would be energy exchange with the wall). Therefore, the microscopic state of the system is constantly changing in time, although this does not affect the macroscopic state. For instance, Fig.1a and Fig.1b depict two different microstates (i.e. different arrangement of particles and different momenta) corresponding to the same macrostate (characterized by density, temperature, pressure, etc.). Since there is no energy exchange with the medium, the total energy of the system is conserved. For the ideal gas, there is only kinetic energy and the elastic bouncing on the walls conserves the magnitude of the velocity of each particle.

Therefore, given a set of initial speeds of the particles, it will be maintained during time. As we will see during the course, there is an intimate connection between the kinetic energy of the particles and the temperature T of a system (this is true on a general base, not only for the ideal gas), with larger T corresponding to faster movement.
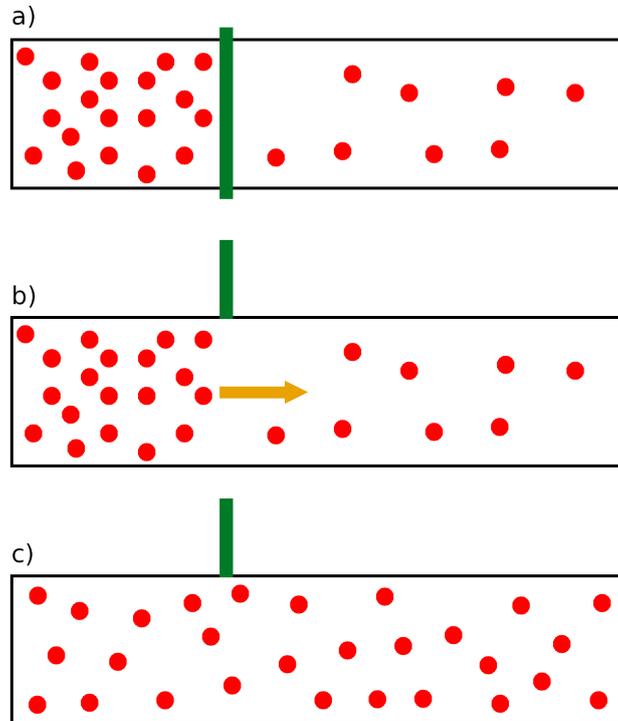

Figure 2: A box containing particles at a certain density ρ_1 is put in contact with a second box characterized by a lower density $\rho_2 < \rho_1$ (a). If one allows particle exchange between the two boxes (b), after a certain time they will both be found at an equilibrium density ρ_{eq} with an intermediate value (c).

Now, let us assume that the system is in contact with a second box characterized by a lower density $\rho_2 \leq \rho_1$ (Fig.2a) and at the same temperature T. The green wall is fixed and prevents heat exchange. Since there is no communication between the two sides, they both keep their thermodynamic state. At a certain point, we remove the green wall (Fig.2b), hence the particles are now free to move between the two boxes. This example is an instance of an *open system*, where there is mass exchange. Due to the difference in density, there will be a net flow from the left to the right, as indicated by the arrow in Fig.2b (note however that this is the *net* flow, i.e. some particles will move from the right to the left, although they will be less than the ones going the other way around). Therefore, both the microscopic and the macroscopic state of the system are now changing in time. If one waits long enough, the density of the two sides will both reach the same value ρ_{eq}, with $\rho_2 \leq \rho_{eq} \leq \rho_1$, and the net flow will be zero: if we

focus just on the portion corresponding to the original box, we will conclude that the system has reached a new equilibrium characterized by a new density. Important note: although there is equilibrium, there will still be a constant exchange of particles between the inside and the outside; it is only the *net* flow that is zero.

Problem. For the system in Fig.2, let us denote the volume of each box as V_1 and V_2, respectively. Under the condition of mass conservation, find the value of ρ_{eq}. Show that in the limit $V_2 \gg V_1$, one has $\rho_{eq} \simeq \rho_2$. The second box in this case acts as a *reservoir*, i.e. it is used to force a thermodynamic state onto the first box.
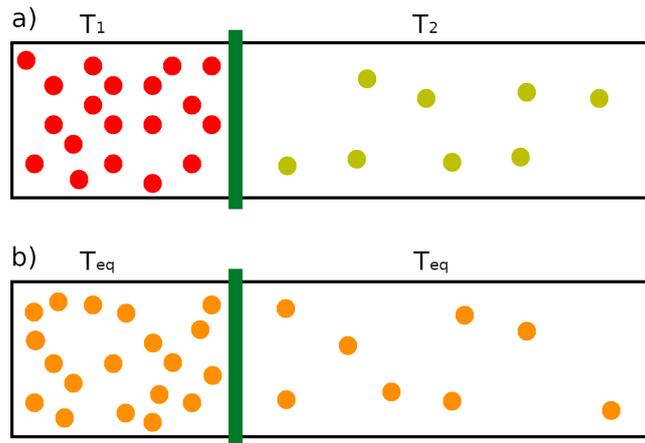

Figure 3: A box containing particles at temperature T_1 is put in contact with a second box characterized by a lower temperature $T_2 < T_1$ (a). If one allows heat exchange through the wall, after a certain time they will both be found at an equilibrium temperature T_{eq} with an intermediate value (b).

As a second example, we consider again two boxes filled with an ideal gas and separated by a wall. Since no exchange of particles is allowed, this is a *closed system*. However, in this case the separating wall is a thermal conductor, meaning that energy can be exchanged between the two boxes as heat. Let us assume that the two boxes are initially at temperatures T_1 and $T_2 < T_1$ (Fig.3a). By exchanging heat, the temperature in the two boxes will change in time, until they both reach the same, equilibrium value T_{eq}, with $T_2 < T_{eq} < T_1$ (Fig.3b).

Finally, we further consider two boxes in contact with temperature T and densities $\rho_1 > \rho_2$ (Fig.4a), where now the green wall is free to move in the horizontal direction (arrow in Fig.4b). By bouncing on the wall, the molecules exert a pressure on it. Hence, the green wall is subjected to a pressure from both sides. However, due to the more dense packing of molecules in box 1, the corresponding pressure p_1 is larger than the one exerted by the particles in box 2, p_2 (intuitively, the bouncing rate grows with the density). As a net effect, there is therefore a pressure $p_1 - p_2$ pushing the wall in the right direction. The wall moves until it reaches a position in which the two pressures are equal to each other (Fig.4c). Note that the final position will depend on a
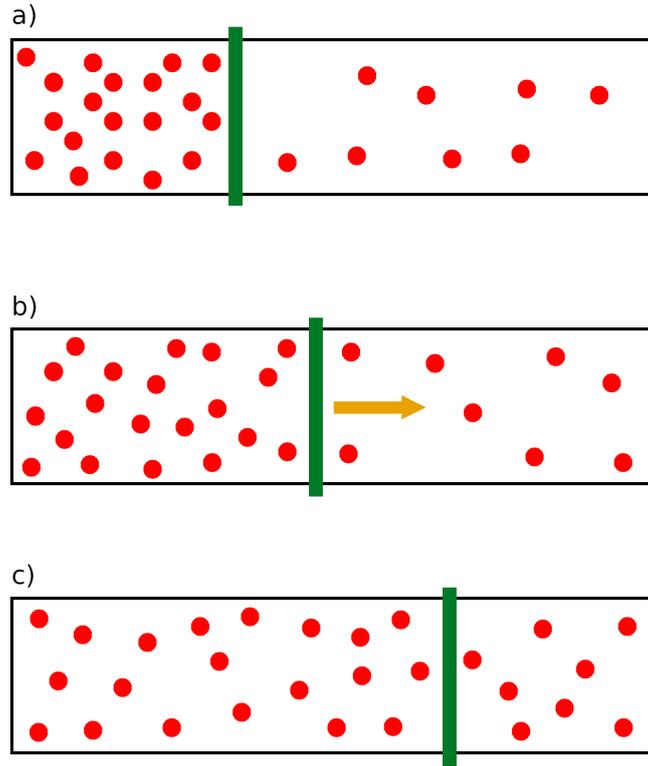
Figure 4: A box containing particles at temperature T and density ρ_1 is put in contact with a second box at the same temperature T and characterized by a lower density $\rho_2 < \rho_1$ (a). If one allows the movement of the wall, the particles in box 1 will exert a larger pressure than the ones in box 2, resulting in the wall moving in the right direction(b). After a certain time, the position of the wall will be such that the values of the pressure on the two sides are equal to each other (c).

key detail of the system, namely on whether the green wall is conducting or isolating, i.e., if heat con be also exchanged. In the first case, the temperature will be the same throughout the whole process (assuming it is slow enough) and the final position of the wall will be such that the density is the same on the two sides. In contrast, if no heat can be exchanged, box 1 is an *isolated system* and its final temperature $T_{f,1}$ will be different from both the initial value T and the final value in box 2, $T_{f,2}$. Particularly, as we will see in a later section, the work done by the particles in box 1 will "pump" energy from box 1 to box 2, thus yielding $T_{f_1} < T < T_{f,2}$.

5 Ideal gas

As mentioned above, the ideal gas is an idealized system in which the particles do not interact with each other. Taking as a reference Fig.1, the particles are constantly moving but, due to the lack of interaction with each other, they just travel through straight lines at constant speed until they reach a wall. In the case of an isolated system, the bouncing is perfectly elastic, so that each particle only changes its direction but not the magnitude of its speed. Real gases can typically be treated as ideal if their density is low enough.
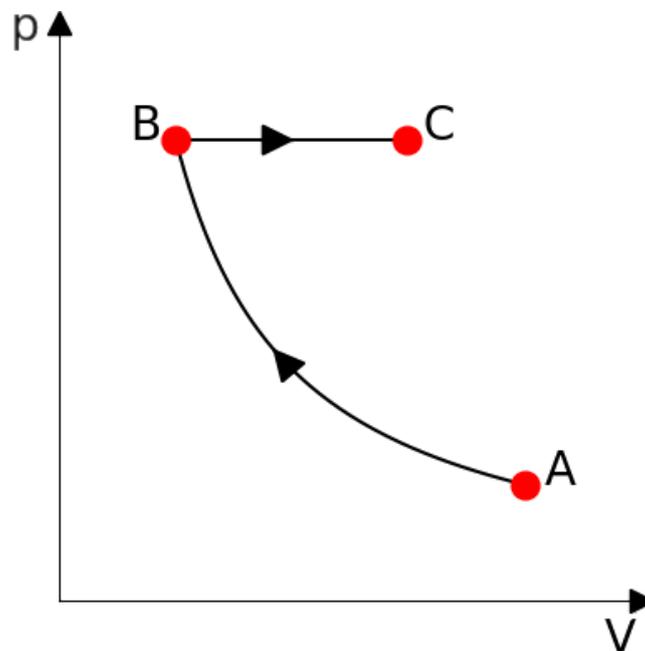
5.1 State equation of an ideal gas

Figure 5: $p - V$ diagram of reversible transformations used to derive the state equation of an ideal gas.

A series of experiments conducted at the dawn of thermodynamics empirically found various relationships involving the pressure p, the volume V and the temperature T of a gas containing n moles, according to the transformation considered:

- **Boyle's law.** Performing a transformation such as the one in Fig.4b at constant T (named *isothermic expansion*), the product between pressure and volume is constant: $p_{\mathrm{ini}}V_{\mathrm{ini}} = p_{\mathrm{fin}}V_{\mathrm{fin}}$, where $p_{\mathrm{ini}}, V_{\mathrm{ini}}$ characterize the initial state and $p_{\mathrm{fin}}V_{\mathrm{fin}}$ the final state.

- **Gay-Lussac's law.** At constant volume (*isochore transformation*), it was found that the relation $p_{\mathrm{ini}}/T_{\mathrm{ini}} = p_{\mathrm{fin}}/T_{\mathrm{fin}}$ holds.

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- **Charles' law.** At constant pressure (*isobaric transformation*), one has $V_{\text{ini}}/T_{\text{ini}} = V_{\text{fin}}/T_{\text{fin}}$.

- **Avogadro's law.** At difference with the other laws, this one does not refer to a transformation, but rather to the microscopic features of ideal gases. It states that, at constant pressure and temperature, the number of moles present in a system is directly proportional to its volume. Therefore, considering two systems at the same pressure and temperature (e.g. the two boxes in Fig.4c in the case of a conducting wall), one has $V_1/n_1 = V_2/n_2$. Due to the relation $N = N_A \cdot n$, the same relation holds when considering the number of molecules N_1, N_2: $V_1/N_1 = V_2/N_2$.

By combining these empirical laws, it is possible to extract a general relation between the state variables of an ideal gas. Let us start by considering a gas containing N molecules and filling a box of volume V_A at pressure p_A and temperature T_A. It is typical to represent the thermodynamic state of the system in the $p - V$ plane, where it is represented as a point (point A in Fig.5). Now, let us perform an isotermic compression towards step B. Assuming the transformation to be slow enough (i.e. it is *reversible*, meaning that it passes through states of equilibrium), the system will travel through a line in the $p - V$ plane which, due to Boyle's law ($p \cdot V =$constant), is shaped as an iperbole. Note however that what really matters here is that the final state is point B, since for the present discussion we are only interested in state variables. By applying Boyle's law, we get

$$p_A V_A = p_B V_B = f_1(T_A, N) \quad T_A = T_B \ , \tag{3}$$

where $f_1(T, N)$ is a certain constant of the isothermic transformation, depending on its temperature and on N, but not on the pressure and volume. After that, we consider as a second transformation a reversible isobaric expansion to a state C, which is represented as a horizontal line in Fig.5. By applying Charles' law, we thus obtain:

$$\frac{V_B}{T_B} = \frac{V_C}{T_C} \quad p_B = p_C \ . \tag{4}$$

From Eq.(3), we can write $V_B = p_A V_A/p_B$ which, substituted in the previous equation and making use of the relations $T_A = T_B$ and $p_B = p_C$, yields $p_A V_A/T_A = p_C V_C/T_C$. State variables do not depend on the particular transformation considered, so that the previous result is a general equality of ideal gases. The constant value of the combination pV/T can depend only on the remaining variable, N, according to a yet unknown function f_2:

$$pV/T = f_2(N) \ . \tag{5}$$

Now let us consider two ideal gases at the same p and T, but characterized by different volumes V_1, V_2 and number of molecules N_1, N_2. According to the formula we just derived, we can write

$$\frac{f_2(N_1)}{f_2(N_2)} = \frac{pV_1/T}{pV_2/T} = \frac{V_1}{V_2} \ . \tag{6}$$

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However, according to Avogadro's law one has $V_1/V_2 = N_1/N_2$, which implies $f_2(N_1)/f_2(N_2) = N_1/N_2$. This is (mathematically) correct for any arbitrary number of molecules. Choosing $N_1 = N$ and $N_2 = 1$, we get $f_2(N) = N \cdot f_2(1)$. Defining the constant $f_2(1) \equiv k_B$, we thus obtain that $f_2(N) = Nk_B$. Substituting in Eq.(5) and rearranging, we finally obtain

$$pV = Nk_BT \ , \tag{7}$$

which is the state equation of gases. k_B is called *Boltzmann's constant* and has a value equal to $k_B \simeq 1.38 \cdot 10^{-23} J/K$. As we will see in the course, k_B is an extremely important constant in soft matter, which determines the role played by temperature in many different phenomena. Making use of the relation $N = N_A n$ and defining $R \equiv N_A \cdot k_B$, the ideal gas equation can also be written as $pV = nRT$. R is called the *gas constant* and has a value equal to $R \simeq 8.31 J/(\text{mol} \cdot K)$.

5.2 Kinetic theory of gases

The central role of k_B can already be appreciated in the case of ideal gases, enabling an interpretation of temperature on a microscopic ground. To this aim, let us consider again the simple case represented in Fig.6a, where the walls are rigid and perfectly isolating. We consider for simplicity a monoatomic gas, meaning that each particle can be represented as a simple point. Let l be the side of the box, which for simplicity is assumed to be cubic. The idea behind the kinetic theory of gases is to derive the pressure by a statistical average of the force applied by the huge amount of molecules composing the system onto each wall. Assuming to have an ideal gas, each molecule will travel in a straight line until it reaches a wall, on which it bounces elastically. Let us focus on a certain molecule i, which is travelling at a certain speed $\boldsymbol{v}_i \equiv (v_{x,i}, v_{y,i}, v_{z,i})$ (here and in the rest of the notes, a **bold** symbol indicates a vectorial quantity; if it is written normally, it means that we are referring to its modulus, e.g. $v_i \equiv |\boldsymbol{v}_i|$). Let us focus on the green wall, and let us consider a reference frame in which the x axis is orthogonal to it. When bouncing elastically against the green wall, the speed of the particle will change in sign along its x coordinate, while the y and z coordinates will be unchanged. Hence, the new speed will be $\boldsymbol{v}'_i \equiv (-v_{x,i}, v_{y,i}, v_{z,i})$ (Fig.6b), i.e. the change in speed upon bouncing will be (in modulus) equal to $2v_{x_i}$. The corresponding change of momentum will have magnitude $2mv_{x_i}$, where m is the mass of a particle.

In order to compute a force f, one has to estimate the change in momentum ΔP observed in a certain time window Δt, so that the force will be obtained as $f = \Delta P/\Delta t$. Since we are interested in statistically-averaged properties, we assume Δt large enough to include many bouncing events. Mathematically, this is implemented by assuming that $\Delta t \gg t_{\text{travel}}$, where t_{travel} is the typical time needed for a particle to travel in the box between two bouncing events on the same wall. If the typical speed of a particle is $<v>$, then one has $t_{\text{travel}} \sim l/<v>$. A note on symbols: $\sim$ indicates a scaling relationship, i.e. a leading-order relationship defined up to a multiplicative constant. In the example above, $t_{\text{travel}} \sim l/<v>$ means that, at the leading order, $t_{\text{travel}} \simeq \text{const} \cdot l/<v>$. In order to compute the total force f_i applied by particle i on
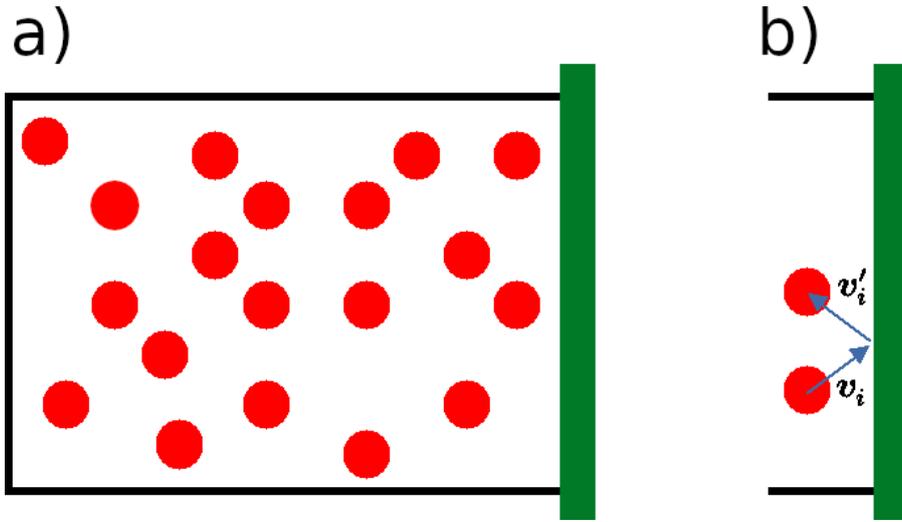
Figure 6: a) Snapshot of a microscopic configuration of an ideal gas. b) Change in the velocity vector after an elastic collision between one molecule and the wall.

the green wall in the time window Δt, we need to compute the total number of times n_{bounces} in which the particle has bounced on the wall. Since the x component of the particle speed is $v_{x,i}$, the time between two bouncing events is $2l/v_{x,i}$, where the factor 2 comes from the fact that the particle has to travel back and forth in order to bounce again on the same wall. The number of bounces occurring in the time window Δt is thus $n_{\text{bounces}} = \Delta t/(2l/v_{x,i}) = v_{x,i}\Delta t/(2l)$. The cumulated change in momentum will thus be $\Delta P_i = 2mv_{x_i} \cdot n_{\text{bounces}} = mv_{x_i}^2\Delta t/l$ Hence, the total force exerted by particle i on the green wall is $f_i = \Delta P_i/\Delta t = mv_{x_i}^2/l$. The total force applied by the gas on the green wall in the same time window is obtained by summing the contributions from all the molecules: $f = \sum_{i=1}^{N} f_i$, i.e.

$$f = \frac{m}{l} \sum_{i=1}^{N} v_{x_i}^2 \; . \tag{8}$$

Our statistical treatment is based under the assumption of overall molecular disorder. This means that, on average, the speed (in a vectorial sense) of the molecules is zero, as there will be half of the molecules travelling in each direction. A more meaningful quantity is the average square of the speed $< v^2 >$, which gives an idea of the typical velocity at which the molecules travel: $< v^2 >= \sum_{i=1}^{N} v_i^2/N$. Note that $v_i^2 = v_{x,i}^2 + v_{y,i}^2 + v_{z,i}^2$, i.e. $< v^2 >=< v_x^2 > + < v_y^2 > + < v_z^2 >$, where $< v_x^2 >= \sum_{i=1}^{N} v_{x_i}^2$ et similia. Since there is no preferred direction in the system, we can safely assume that $< v_x^2 >=< v_y^2 >=< v_z^2 >$, i.e. they are all equal to $< v^2 > /3$. Since $\sum_{i=1}^{N} v_{x_i}^2 = N < v_x^2 >$, from Eq.(8) one has

$$f = \frac{Nm < v^2 >}{3l} \; . \tag{9}$$

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The pressure p exerted by the gas on the wall is easily computed as the ratio between the force and the surface of the wall (which is equal to l^2):

$$p = \frac{f}{l^2} = \frac{Nm < v^2 >}{3V} \ , \tag{10}$$

where $V = l^3$ is the volume of the box. From the state equation of gases, one has also $p = Nk_BT/V$, so that $k_BT = m < v^2 > /3$. Rearranging, we finally find:

$$\frac{3}{2}k_BT = \frac{1}{2}m < v^2 > \ . \tag{11}$$

On the right-hand side of the previous formula, we can recognize the average kinetic energy of a particle. Therefore, Eq.(11) states that for a monoatomic ideal gas *the temperature is directly proportional to the average kinetic energy of a molecule*, thus providing a direct microscopic interpretation of temperature. This result has been derived here for the simplest case of a monoatomic simple gas, but **it holds in general**. As a matter of fact, it is a special case of the *equipartition theorem of energy*, which states that each quadratic term in the energy of a system yields on average a contribution equal to $k_BT/2$ per particle. In the case of a monoatomic ideal gas, the energy per particle is simply $E = mv^2/2 = m(v_x^2 + v_y^2 + v_z^2)$, so there are three quadratic terms each contributing $k_BT/2$ yielding an average kinetic energy per particle equal to $3 \cdot k_BT/2$. As a more complex example, in a diatomic ideal gas each molecule can be represented as two points joined by a rigid stick. In this case, the kinetic energy has a contribution coming from the translational motion (three quadratic terms as in the case of the monoatomic gas) and another coming from the rotational motion, which includes two quadratic terms. In this case, the average kinetic energy per molecule will thus be $(5/2)k_BT$.

    Problem. A more realistic approach to model a diatomistic gas is to account for the vibration of the bond joining the two points. Therefore, instead of assuming it to be a rigid stick, one can model a molecule as two points joined by a spring with elastic constant k_s and equilibrium distance d_0. 1) According to the equipartition theorem, what is the average energy stored in a molecule according to this model? Remember to account for the three-dimensionality of the problem. 2) Starting from the equipartition theorem, estimate the typical size of displacement from the equilibrium distance. How does it change with increasing temperature? How does it change with increasing k_s?

6 Thermodynamic transformations

Armed with the equation of state of the ideal gases, we now proceed to study some basic thermodynamic transformations. The key point of the present section is to show, by means of practical examples, that energy exchange as work or heat is transformation-dependent and can thus not be associated to a state variable.

6.1 The internal energy is a state variable

It is important to stress that *the internal energy is a state variable*, since it is computed by summing up the kinetic energy and the interactions within the system, which depend only on the particular equilibrium state under consideration. In the particular case of a monoatomic ideal gas, the only contribution comes from the translational kinetic energy, thus

$$E = \frac{1}{2}Nm < v^2 >= \frac{3}{2}Nk_BT \tag{12}$$

where we set the arbitratry zero of the internal energy to the zero of the kinetic energy.

6.2 Isochore transformation

The first and simplest example of thermodynamic transformation is provided by a isochore transformation, where the temperature of the system is changed while keeping the volume fixed. In the $p - V$ diagram, this transformation is depicted as a vertical line. This can be easily achieved by considering a box with rigid, conducting walls. As an example, let us consider a box containing N molecules of a gas and with volume V. The box is at equilibrium with the environment at a certain temperature T_A. The pressure can be easily computed by means of the equation of state, Eq.(7), and is equal to $p_A = Nk_BT_A/V$. At a certain point, we start slowly heating the environment (and the box) until a temperature $T_B > T_A$ is reached. Since the walls are rigid, the volume of the box is again V. By means of Eq.(7), we thus obtain that the new value of the pressure is $p_B = Nk_BT_B/V > p_A$. We note that the gas performs no work, since there is no displacement of the walls (see below for a different case), $\Delta W = 0$. By combining the first law of thermodynamics, Eq.(1), with Eq.(12), we thus conclude that $\Delta Q = \Delta E = (3/2)Nk_B(T_B - T_A) > 0$, where the positive sign indicates that the system is absorbing heat from the environment during the temperature increase. To summarize, for the isochore transformation and a monoatomic ideal gas, one has

$$\Delta Q = \Delta E = \frac{3}{2}Nk_B(T_B - T_A), \qquad \Delta W = 0 . \tag{13}$$

6.3 Isobaric expansion

Another simple example of thermodynamic transformation is provided by a isobaric expansion. In Fig.7a, we consider an ideal gas with N molecules and contained in a box with conducting
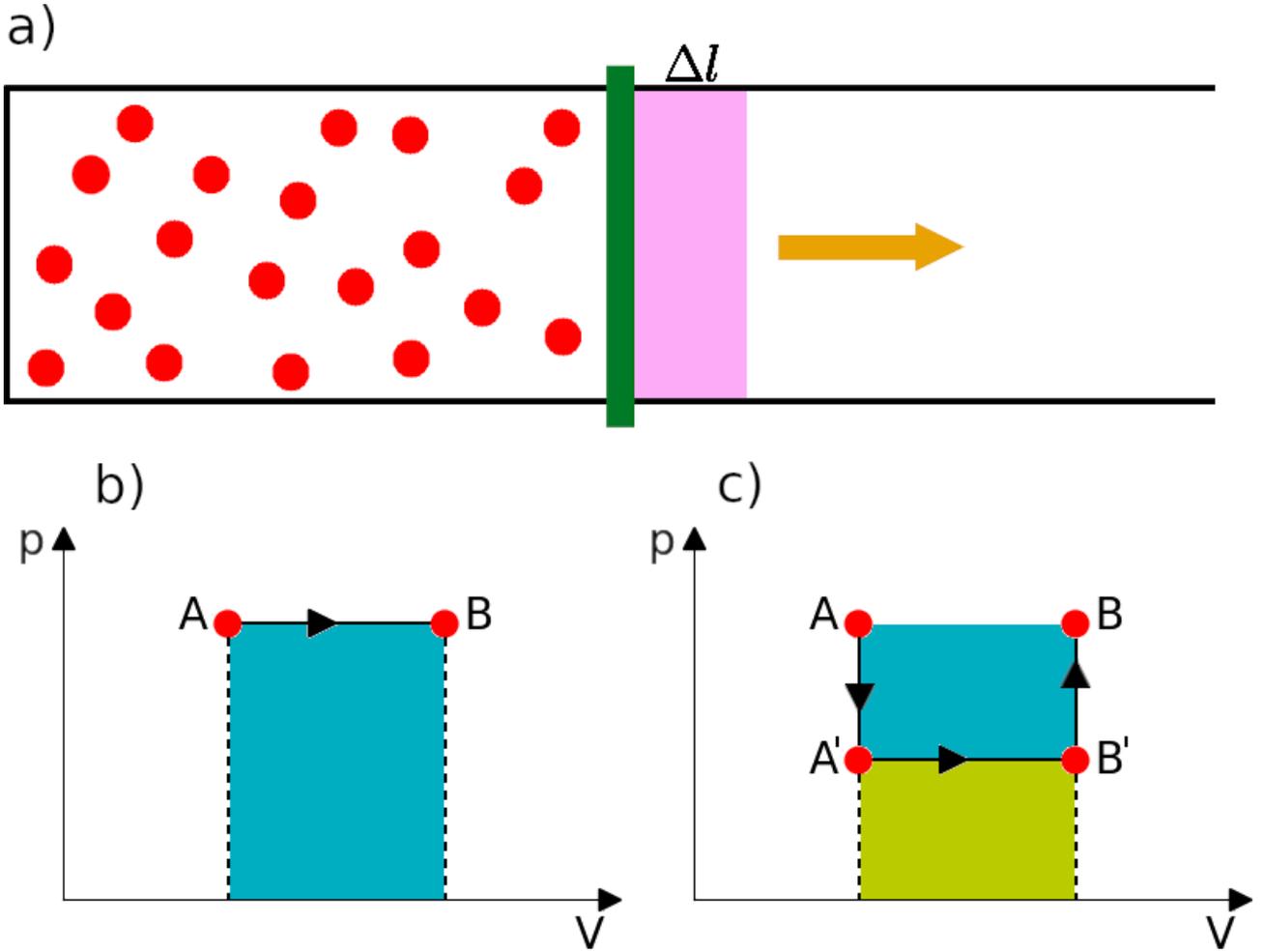
Figure 7: a) Snapshot of a microscopic configuration of an ideal gas. b) Change in the velocity vector after an elastic collision between one molecule and the wall.

walls. The green wall has an area equal to s and is mobile. On the other side of the wall, there is a constant pressure p_A being exerted by the environment (e.g. the atmospheric pressure), which has temperature T_A. The system is at equilibrium with the environment, so that its pressure and temperature are equal to p_A and T_A, respectively. The volume is determined by these conditions by means of the equation of state, Eq. (7), and is equal to $V_A = Nk_BT_A/p_A$. By means of suitable reversible thermodynamic transformations, we want to change the state of the system to point B, characterized by $V_B > V_A$ and $p_B = p_A$. We consider two different scenarios.

In the first scenario (Fig.7b), the target state is imposed by an isobaric expansion. This for instance can be achieved by slowly heating up the environment in order to increase its temperature (and the temperature of the box) up tp $T_B = p_BV_B/(Nk_B)$. The mobile wall

ensures that the pressure is always counterbalancing the one of the environment, which in this example is always equal to p_A, so that $p = p_A$ throughout the whole process and the transformation can be depicted as a horizontal line in the $p-V$ plane (Fig.7b). In the expansion process, the gas does some work ΔW. What is the value of ΔW? In order to answer this question, let us recall that the work is computed as the scalar product between the force applied by the gas $\boldsymbol{f}$ and the displacement vector $\Delta \boldsymbol{l}$ (Fig.7a), $\Delta W = -\boldsymbol{f} \cdot \Delta \boldsymbol{l}$. Note that we have added a minus sign due to the convention used in these notes, according to which the work is negative whenever it is performed by the system. Since both the force and the displacement vector have the same direction (right direction in Fig.7a), one can simply write $\Delta W = -f \cdot \Delta l$. Since we are working in isobaric conditions, the force at any point along the transformation is constant and can be computed as $f = p_A \cdot s$, while the displacement satisfies the condition $s \cdot \Delta l(V) = V - V_A$ (pink region in Fig.7a), i.e. $\Delta l(V) = (V - V_A)/s$. The work performed by the gas to reach state B is thus $-f \cdot \Delta l(V_B) = -p_A \cdot (V_B - V_A) \equiv -p_A \cdot \Delta V$, which corresponds in magnitude to the area below the transformation line, coloured in blue in Fig.7b. We note that, during the process, the box also exchanges heat with the environment. By means of Eq.(1), we can compute the heat exchanged as $\Delta Q = \Delta E - \Delta W = \Delta E + p_A \Delta V$. As in the case of the isochore transformation, the change in internal energy can be computed from Eq.(12) as $\Delta E = (3/2)Nk_B(T_B - T_A)$. Therefore, we conclude that

$$\Delta Q = \frac{3}{2}Nk_B(T_B - T_A) + p_A \Delta V \qquad \Delta W = p_A \Delta V \ . \qquad (14)$$

As a second scenario, we consider the chain of transformations represented in Fig.7c. The first step $(A \to A')$ is an isochore transformation in which the gas is cooled to a temperature $T_{A'}$. In this case, the same results as in Eq.(13) hold: $\Delta Q_{A \to A'} = \Delta E_{A \to A'} = -(3/2)Nk_B(T_A - T_{A'}) < 0$ and $\Delta W_{A \to A'} = 0$. The second step $(A' \to B')$ consists in an isobaric expansion at pressure $p_{A'}$, for which $\Delta W_{A' \to B'} = p_{A'}(V_{B'} - V_{A'}) > 0$, $\Delta E_{A' \to B'} = (3/2)Nk_B(T'_B - T_{A'}) > 0$ and $\Delta Q_{A' \to B'} = (3/2)Nk_B(T'_B - T_{A'}) + p_{A'}(V_{B'} - V_{A'})$ (see Eq.(14)). Finally, in the third step $(B' \to B)$ a second isochore transformation is considered, in which the gas is heated from $T_{B'}$ to T_B. Applying again Eq.(13), we find $\Delta Q_{B' \to B} = \Delta E_{B' \to B} = (3/2)Nk_B(T_B - T_{B'}) > 0$ and $\Delta W_{B' \to B} = 0$. The overall change in internal energy is obtained as $\Delta E = \Delta E_{A \to A'} + \Delta E_{A' \to B'} + \Delta E_{B' \to B} = -(3/2)Nk_B(T_A - T_{A'}) + (3/2)Nk_B(T'_B - T_{A'}) > 0 + (3/2)Nk_B(T_B - T_{B'}) = (3/2)Nk_B(T_B - T_A)$, which is exactly the same result that we obtained in the first scenario, Eq.(14). This is as expected, since the internal energy is a state variable and its overall change does not depend on the particular set of transformations employed, but only on the initial and final state, which are A and B for both Fig.7b and Fig.7c. In contrast, the total work performed by the gas is $\Delta W = \Delta W_{A \to A'} + \Delta W_{A' \to B'} + \Delta W_{B' \to B} = 0 + p_{A'}(V_{B'} - V_{A'}) + 0$. Remembering that $V_{A'} = V_A$ and $V_{B'} = V_B$, we finally get $\Delta W = p_{A'}(V_B - V_A)$, which corresponds to the area depicted in green in Fig.7c and is evidently different than the value obtained in the first scenario (Eq.(14) and blue region in Fig.7). A similar conclusion holds for the total heat exchanged: $\Delta Q = \Delta Q_{A \to A'} + \Delta Q_{A' \to B'} + \Delta Q_{B' \to B} = -(3/2)Nk_B(T_A - T_{A'}) + (3/2)Nk_B(T'_B - T_{A'}) + p_{A'}(V_{B'} - V_{A'}) + (3/2)Nk_B(T_B - T_{B'}) = (3/2)Nk_B(T_B - T_A) - p_{A'}(V_B - V_A)$, which is

different than the result obtained in Eq.(14). Therefore, despite sharing the same initial and final point, *the heat and work exchanged by the system and the environment depend on the particular transformations considered.*
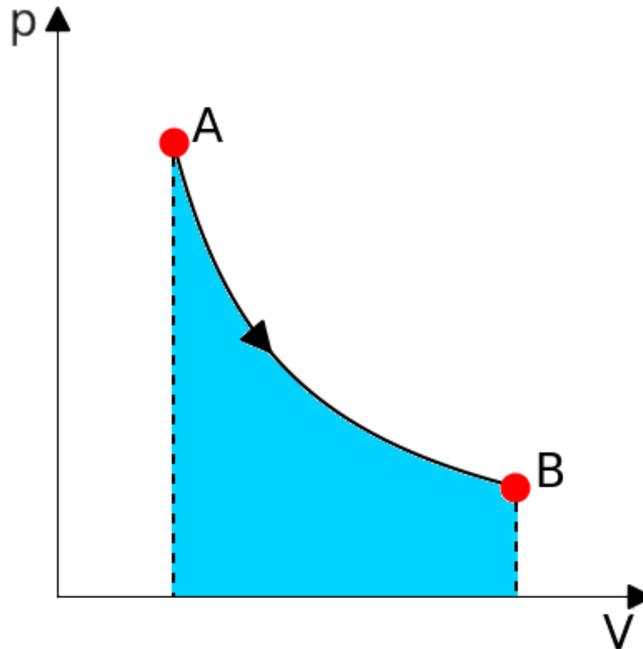
6.4   Isothermic expansion

Figure 8: $p - V$ diagram of an isothermic expansion.

An isothermic expansion can be obtained with a similar setup as for the isobaric case: a gas is contained in a box with conductive walls (one of which mobile) and in contact with a reservoir with temperature T_A and pressure p_A (Fig.8). After equilibration has been attained, the pressure of the reservoir is changed slowly down to a value p_B, while keeping the same value of the temperature. This case is presented here because it introduces some complications in the calculations. Our aim is again to compute $\Delta E, \Delta Q$ and ΔW. As for the internal energy, since the transformation is isothermic there is no change in temperature, hence $\Delta E = 0$ (compare Eq.(12)). As for the work performed by the gas, the same considerations as in for isobaric expansion hold. Nevertheless, in the present case the pressure is not constant, so that one has to integrate the infinitesimal work done around each point along the transformation. Particularly, the infinitesimal work reads here $p(V)dV$, where p depends on the volume according to the state equation $p = Nk_BT_A/V$ (remember that $T = T_A$ throughout the whole transformation). The total work is thus

$$\Delta W = -\int_{V_A}^{V_B} \frac{Nk_BT_A}{V}dV = -Nk_BT_A \ln \frac{V_B}{V_A} < 0 \; , \tag{15}$$

which corresponds in magnitude to the area depicted in cyan in Fig.8. By following the convention adopted in these notes, the minus sign indicates that the work is performed by the gas (inverting the direction of the transformation one would obtain $\Delta W > 0$, which is the correct outcome for an isothermic compression). Applying the first law of thermodynamics, the heat exchanged is thus $\Delta Q = \Delta E - \Delta W = 0 + Nk_BT_A \ln \frac{V_B}{V_A} = Nk_BT_A \ln \frac{V_B}{V_A} > 0$. Therefore, during a reversible isothermic expansion the gas absorbs heat from the environment and transforms it completely into work.
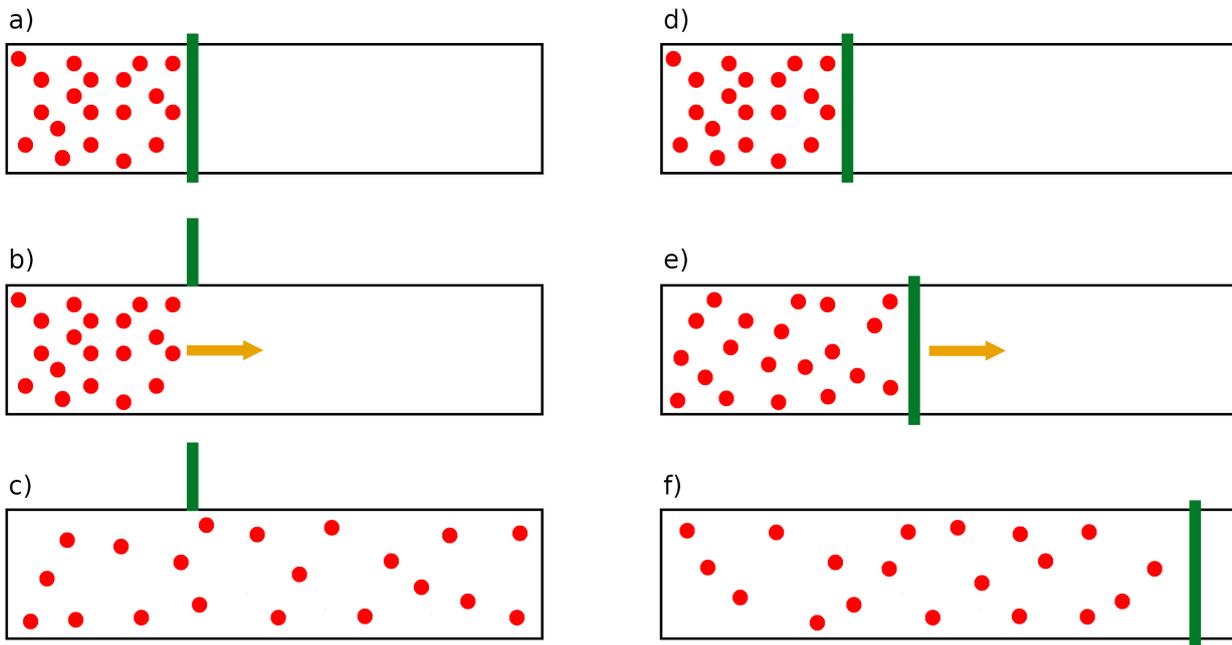
6.5   Adiabatic transformation

Figure 9: Starting from a gas enclosed in a small volume (a), an irreversible adiabatic expansion can be obtained by removing one wall and letting the molecules diffuse freely in a larger volume (b,c). From the same starting point (d), a reversible adiabatic transformation can be obtained by letting the green wall move (e) and slowly changing the external pressure to its final value (f), chosen such that the same final volume as for the irreversible expansion is obtained.

For completeness, we also mention the adiabatic transformations, in which the gas cannot exchange heat with the environment (isolating walls). In this case, $\Delta Q = 0$, so that the first law dictates that $\Delta W = \Delta E = Nk_B\Delta T$. Adiabatic transformations provide a good playground to compare reversible and irreversible transformations.

In the left column of Fig.9, we consider an irreversible adiabatic transformation. The gas is enclosed in a box of volume V_A by isolating walls (Fig.9a). Then, the green wall is removed,

and the gas can expand in a larger box with volume V_B, where the walls are again isolated from the outside (Fig.9b). Immediately after the removal of the wall, the gas is out of equilibrium, since it is not uniformely distributed in the available volume. Eventually, the gas reaches equilibrium by diffusion (Fig.9c). In this case, we notice that no work is performed by or onto the gas (the wall has just been removed from the outside), hence $\Delta W = 0$. Since also $\Delta Q = 0$, we conclude that $\Delta E = 0$, so that there is no temperature change. This irreversible adiabatic transformation is also an isotherm! This simultaneous isotherm-adiabatic character can be proven to be impossible for reversible transformations. As a further note, we stress that irreversible transformations cannot be drawn in the $p-V$ diagram, since the intermediate states are out of equilibrium and do not correspond to any point on it. In this case, one can only draw the starting and final equilibrium points. In some books the transformation is represented by simply joining the two points with a dashed line, to indicate the absence of intermediate equilibrium points.

In the right column of Fig.9, instead of removing the wall, we make it mobile and let the gas push it slowly by almost counterbalancing its pressure step by step, until it reaches the same final volume V_B considered in the irreversible case, at which point we counterbalance the pressure exactly. In this case, the gas is doing some work, so that we expect that $\Delta W < 0$. Since $\Delta E = \Delta W$ for adiabatic transformations, we also expect that $\Delta E < 0$, implying that the temperature of the gas will lower upon expansion, which is in remarkable contrast with the free expansion considered above. Quantitatively, we consider an infinitesimal reversible transformation for which the work is pdV and $dE = (3/2)Nk_BdT$, implying $pdV = (3/2)Nk_BdT$. Due to the equation of state, we can write $p = Nk_BT/V$, hence $Nk_BT \cdot dV/V = (3/2)Nk_BdT \Rightarrow dV/V = (3/2)dT/T$. We thus have:

$$\int_{V_A}^{V_B} \frac{dV}{V} = \frac{3}{2}\int_{T_A}^{T_B} \frac{dT}{T} \ , \tag{16}$$

that is

$$\frac{V_B}{V_A} = \left(\frac{T_B}{T_A}\right)^{\frac{3}{2}} \ . \tag{17}$$

Therefore, we can write $T_B = T_A \cdot (V_B/V_A)^{-2/3}$. If $V_B > V_A$, the gas is expanding (such as in the case studied here) and $T_B < T_A$: the work done by the gas is performed at the expense of its internal energy! In the case of compression, $V_B < V_A$ and $T_B > T_A$: the gas uses the compression work to increase its internal energy.

6.6 Thermodynamic cycles

A special class of transformations are the *thermodynamic cycles*, in which the initial and final state are the same. Thermodynamic cycles are historically very important, since they constitute the practical way in which useful work can be extracted from a heat source. Here, we consider two examples of reversible thermodynamic cycles working between two sources at fixed temperatures T_A and $T_C < T_A$, as reported in Fig.10.
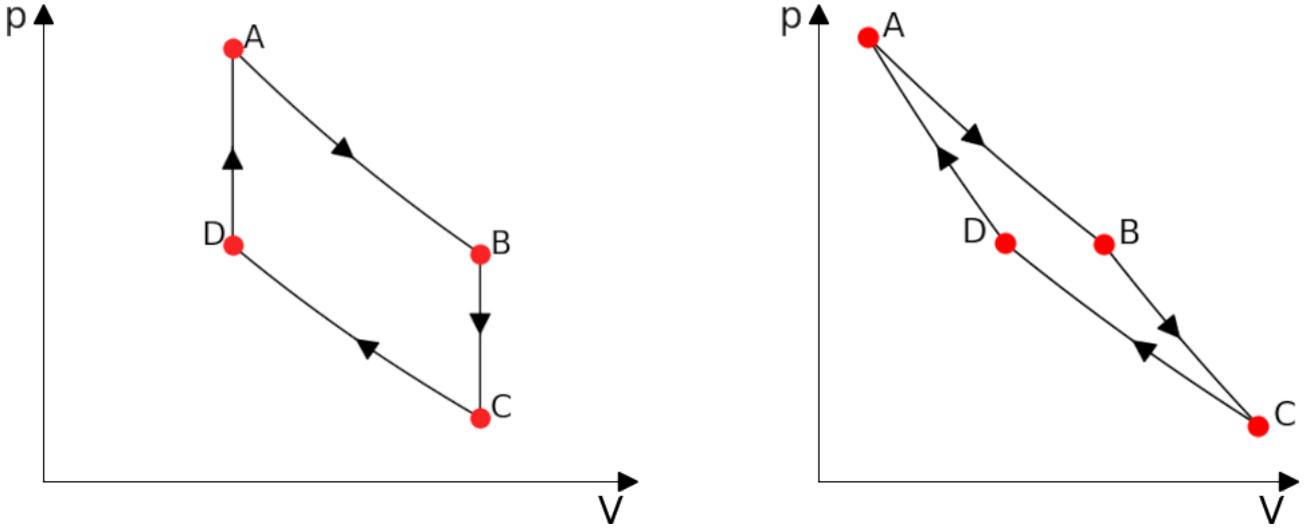
Figure 10: Examples of reversible thermodynamic cycles. Left: the Stirling cycle is obtained by combining isothermic (expansion AB and compression CD) and isochore (BC and DA) transformations. Right: the Carnot cycle is composed of two isothermic (expansion AB and compression CD) and two adiabatic (expansion BC and compression DA) transformations.

6.6.1 Stirling Cycle

In the left panel of Fig.10 we depict a cycle consisting of alternating isothermic and isochore transformations (Stirling cycle). We use as a reference the volume and temperature at two opposite points of the cycle, namely A and C, and derive the rest of quantities as a function of these two state variables and of the number N of molecules in the system. Moreover, we assume that the system is an ideal monoatomic gas.

- **$A \rightarrow B$.** In this isothermic expansion, the work is computed by means of Eq.(15) as $\Delta W_{AB} = -Nk_B T_A \ln(V_B/V_A)$. Since $V_B = V_C > V_A$, we thus have

$$\Delta W_{AB} = -Nk_B T_A \ln\left(\frac{V_C}{V_A}\right) < 0 \ . \tag{18}$$

where the minus sign indicates that the work is being done by the system. Since the transformation is isothermic, one has $T_B = T_A$, so that there is no change in internal energy:

$$\Delta E_{AB} = (3/2)Nk_B(T_B - T_A) = 0 \ . \tag{19}$$

Finally, the heat exchanged is computed from the first law as

$$\Delta Q_{AB} = -\Delta W_{AB} = Nk_B T_A \ln\left(\frac{V_C}{V_A}\right) > 0 \ . \tag{20}$$

$\Delta Q_{AB} > 0$ implies that the system is absorbing heat. This makes sense from a physical perspective: in this step, the system is in contact with the hot source and converts the absorbed heat into work.

- **$B \to C$.** In an isochore transformation, no work is done, so that

$$\Delta W_{BC} = 0 \ . \tag{21}$$

The change in internal energy is $\Delta E_{BC} = (3/2)Nk_B(T_C - T_B)$. Since $T_B = T_A > T_C$, we get

$$\Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 \ . \tag{22}$$

Hence, the system is cooling during BC. From the first law, we also have

$$\Delta Q_{BC} = \Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 \ , \tag{23}$$

so that in this step the system releases heat into the environment. Physically, this steps represents the cooling of the system upon contact with the cold source (more precisely, with an infinite set of sources with infinitesimally-decreasing temperature, so as to ensure the reversibility of the process).

- **$C \to D$.** In this isothermic compression, the work is computed again as $\Delta W_{CD} = -Nk_BT_C \ln(V_D/V_C)$. Since $V_D = V_A < V_C$, we have

$$\Delta W_{CD} = Nk_BT_C \ln\left(\frac{V_C}{V_A}\right) > 0 \ . \tag{24}$$

The work is positive, since it is being done onto the system. This transformation is isothermic, so that the change in internal energy is $\Delta E_{CD} = 0$. Finally, the heat exchanged is computed from the first law as

$$\Delta Q_{CD} = -\Delta W_{CD} = -Nk_BT_C \ln\left(\frac{V_C}{V_A}\right) < 0 \ . \tag{25}$$

$\Delta Q_{CD} < 0$ implies that the system is releasing heat into the environment. Physically, this step is necessary to bring the system back to its initial volume, which is done at the expense of "wasting" energy by releasing it into the cold source.

- **$D \to A$.** This is another isochore transformation, therefore

$$\Delta W_{DA} = 0 \ . \tag{26}$$

The change in internal energy is $\Delta E_{DA} = (3/2)Nk_B(T_A - T_D)$. Since $T_D = T_C < T_A$, we have

$$\Delta E_{DA} = \frac{3}{2}Nk_B(T_A - T_C) > 0 \ . \tag{27}$$

Hence, the system is increasing its temperature. Again, the heat exchanged is computed from the first law, yielding:

$$\Delta Q_{DA} = \Delta E_{DA} = \frac{3}{2} N k_B (T_A - T_C) > 0 \, , \tag{28}$$

so that the system is absorbing heat from the environment.

We are now ready to compute the final values of the energy exchanges. For the internal energy, we have $\Delta E = \Delta E_{AB} + \Delta E_{BC} + \Delta E_{CD} + \Delta E_{DA}$, which gives

$$\Delta E = 0 - \frac{3}{2} N k_B (T_A - T_C) + 0 + \frac{3}{2} N k_B (T_A - T_C) = 0 \, . \tag{29}$$

This is expected, since the internal energy is a state variable and in the cycle the initial and final state are the same. Now, as for the work, we have $\Delta W = \Delta W_{AB} + \Delta W_{BC} + \Delta W_{CD} + \Delta W_{DA}$, i.e.

$$\Delta W = -N k_B T_A \ln\left(\frac{V_C}{V_A}\right) + 0 + N k_B T_C \ln\left(\frac{V_C}{V_A}\right) + 0 = -N k_B (T_A - T_C) \ln\left(\frac{V_C}{V_A}\right) < 0 \, . \tag{30}$$

The work is negative, i.e. as a net result the system is doing work. Quantitatively, its magnitude is equal to the area enclosed by the cycle, which is true for all thermodynamic cycles obtained via reversible transformations.

The heat can be computed in the same way as $\Delta Q = \Delta Q_{AB} + \Delta Q_{BC} + \Delta Q_{CD} + \Delta Q_{DA}$. However, there is a faster route. Indeed, the first law applies to any transformation, including a cycle like the one we are studying. Since $\Delta E = 0$, we have $\Delta Q = -\Delta W = N k_B (T_A - T_C) \ln(V_C / V_A) > 0$, i.e. as a net effect the system is absorbing heat. It is worth further discussing the heat exchange. Particularly, we have shown that the system absorbs heat in the steps AB and DA, while it releases heat in the steps BC and CD. Let us denote as $\Delta Q_a = \Delta Q_{AB}$ the heat adsorbed from the hot source (at temperature T_A) and as $\Delta Q_r = \Delta Q_{CD}$ the heat released into the cold source (T_C). The *efficiency* η of the cycle is defined as the ratio between the work produced and the heat absorbed, $\eta \equiv |\Delta W / \Delta Q_a|$, where the absolute value is introduced to yield a positive value of η. The idea is that a machine operating through a cycle absorbs energy from hot sources and converts part of it into work, while another part is lost as heat released to the cold sources, so that $0 \leq \eta \leq 1$. The efficiency gives a measure of how good is the machine in performing its task. In the present case, we get

$$\eta = \frac{N k_B (T_A - T_C) \ln\left(\frac{V_C}{V_A}\right)}{N k_B T_A \ln\left(\frac{V_C}{V_A}\right)} = 1 - \frac{T_C}{T_A} \, . \tag{31}$$

Remarkably, the efficiency for the Stirling cycle depends only on the temperature of the two sources. Important note: in the isochore transformations, there is also heat exchange. Particularly, the system absorbs heat in the step DA. In order to obtain a reversible transformation,

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when the system is in point C one cannot put it directly in contact with the hot source (T_A), but has to ideally consider an infinite set of sources with slowly-increasing temperatures $T_C + dT, T_C + 2dT, \ldots$. Similarly, in the step BC the cooling has to happen by considering the same set of infinite temperatures in the other direction. As a net effect, each of these intermediate sources will have exchanged zero energy with the system, and that is why they are not included in the computation of η. In contrast, along the isotherms there is a net exchange with the hot and cold sources.

6.6.2 Carnot Cycle

The Carnot cycle (right panel of Fig.10) consists of alternating isothermic and adiabatic transformations. A similar procedure as for the Stirling cycle can be implemented, although it has to be adjusted to account for the adiabatic transformations. Particularly, from Eq.(17) we have $V_B = V_C(T_A/T_C)^{3/2}$ and $V_D = V_A(T_C/T_A)^{3/2}$.

- **$A \rightarrow B$.** In this isothermic expansion, the work is computed by means of Eq.(15) as $\Delta W_{AB} = -Nk_B T_A \ln(V_B/V_A)$. Since $V_B = V_C(T_A/T_C)^{3/2} > V_C > V_A$, we thus have

$$\Delta W_{AB} = -Nk_B T_A \ln\left[\frac{V_C}{V_A}\left(\frac{T_A}{T_C}\right)^{\frac{3}{2}}\right] < 0 . \tag{32}$$

where the minus sign indicates that the work is being done by the system. Since the transformation is isothermic, one has $T_B = T_A$, so that there is no change in internal energy:

$$\Delta E_{AB} = (3/2)Nk_B(T_B - T_A) = 0 . \tag{33}$$

Finally, the heat exchanged is computed from the first law as

$$\Delta Q_{AB} = -\Delta W_{AB} = Nk_B T_A \ln\left[\frac{V_C}{V_A}\left(\frac{T_C}{T_A}\right)^{\frac{3}{2}}\right] > 0 . \tag{34}$$

$\Delta Q_{AB} > 0$ implies that the system is absorbing heat.

- **$B \rightarrow C$.** In an adiabatic transformation, there is no heat exchange:

$$\Delta Q_{BC} = 0 . \tag{35}$$

The change in internal energy is $\Delta E_{BC} = (3/2)Nk_B(T_C - T_B)$. Since $T_B = T_A > T_C$, we get

$$\Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 . \tag{36}$$

Hence, the system is cooling during BC. From the first law, we also have

$$\Delta W_{BC} = \Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 , \tag{37}$$

so that in this step the system is doing work.

- **$C \to D$.** In this isothermic compression, the work is computed by means of Eq.(15) as $\Delta W_{CD} = -Nk_B T_C \ln(V_D/V_C)$. Since $V_D = V_A(T_C/T_A)^{3/2} < V_A < V_C$, we thus have

$$\Delta W_{CD} = Nk_B T_C \ln \left[\frac{V_C}{V_A} \left(\frac{T_A}{T_C} \right)^{\frac{3}{2}} \right] > 0 \ . \tag{38}$$

where the positive sign indicates that the work is being done onto the system. Since the transformation is isothermic, one has $T_D = T_C$, so that there is no change in internal energy:

$$\Delta E_{CD} = 0 \ . \tag{39}$$

Finally, the heat exchanged is computed from the first law as

$$\Delta Q_{CD} = -\Delta W_{CD} = -Nk_B T_C \ln \left[\frac{V_C}{V_A} \left(\frac{T_A}{T_C} \right)^{\frac{3}{2}} \right] < 0 \ . \tag{40}$$

$\Delta Q_{CD} < 0$ implies that the system is releasing heat.

- **$D \to A$.** This is another adiabatic transformation, so that there is no heat exchange:

$$\Delta Q_{DA} = 0 \ . \tag{41}$$

The change in internal energy is $\Delta E_{DA} = (3/2)Nk_B(T_A - T_D)$. Since $T_D = T_C < T_A$, we get

$$\Delta E_{DA} = \frac{3}{2} Nk_B(T_A - T_C) > 0 \ , \tag{42}$$

as expected from a heating process. From the first law, we also have

$$\Delta W_{DA} = \Delta E_{DA} = \frac{3}{2} Nk_B(T_A - T_C) > 0 \ , \tag{43}$$

so that in this step work is being done onto the system (adiabatic compression).

The total work is negative (i.e. it is performed by the system) and equal in magnitude to the area enclosed within the cycle. Quantitatively, we have

$$\Delta W = \Delta W_{AB} + \Delta W_{BC} + \Delta W_{CD} + \Delta W_{DA} = -Nk_B(T_A - T_C) \ln \left[\frac{V_C}{V_A} \left(\frac{T_A}{T_C} \right)^{\frac{3}{2}} \right] < 0 \ . \tag{44}$$

In contrast with the Stirling cycle, here there is heat exchange only along the isotherms. It is thus evident that there is a net absorption of heat from the hot source (T_A) and a net release

of heat from the cold source (T_C). The adsorbed heat corresponds to $\Delta Q_a = \Delta Q_{AB}$, hence the efficiency reads

$$\eta = \frac{Nk_B(T_A - T_C)\ln\left[\frac{V_C}{V_A}\left(\frac{T_A}{T_C}\right)^{\frac{3}{2}}\right]}{Nk_BT_A\ln\left[\frac{V_C}{V_A}\left(\frac{T_C}{T_A}\right)^{\frac{3}{2}}\right]} = 1 - \frac{T_C}{T_A} \ . \tag{45}$$

In spite of being qualitatively different, both for the Stirling and for the Carnot cycle the efficiency is the same, and is determined only by the temperature of the two sources in thermal contact with the system. This is not a coincidence, but rather a consequence of the second law of thermodynamics by means of Carnot's theorem, as will be discussed below.
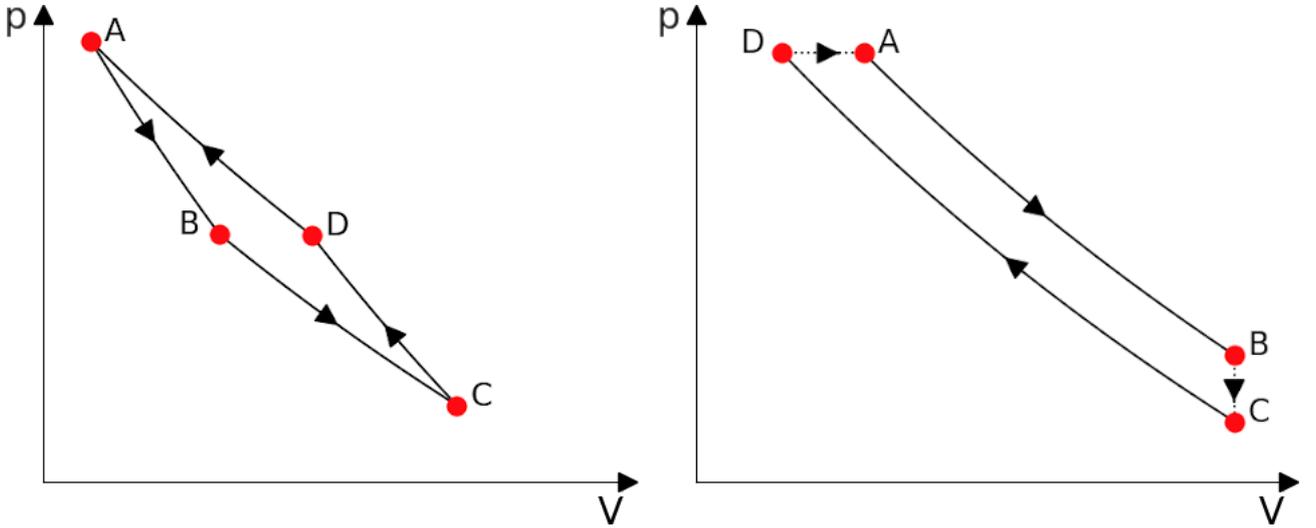
6.6.3 Refrigeration and irreversible cycles

Figure 11: Left: the inverted Carnot cycle uses external work to pump energy from a cold to a heat source. Right: example of irreversible cycle, obtained by modifying the adiabatic expansion into an isochore cooling (transformation BC).

Reversible cycles can be inverted and yield an overall energy exchange with same magnitude but opposite sign. For instance, in the left panel of Fig.11 we depict an inverted Carnot cycle, for which the total work is

$$\Delta W = Nk_B(T_A - T_C)\ln\left[\frac{V_C}{V_A}\left(\frac{T_A}{T_C}\right)^{\frac{3}{2}}\right] > 0 \ , \tag{46}$$

i.e. energy is being delivered to the system by means of external work. By following the same steps as in the previous section, it is easy to show that in the inverted Carnot cycle the heat is

adsorbed from the cold source (T_C) during step BC, while it is released to the hot source (T_D) during step DA. Hence, in this cycle the heat flow goes against its "natural" direction thanks to the energy pumped in by the external work. This kind of cycles are called *refrigeration cycles.*

In the right panel of Fig.11, we further consider a cycle in which two of the transformations are irreversible. Particularly, we consider a standard Carnot cycle in which the adiabatic transformations BC and DA are substituted by an irreversible isochore cooling and an irreversible isobaric expansion, respectively. This can be realized in practice by putting the system in direct thermal contact with the source at constant volume (or pressure), rather than gently cooling (heating) it via the adiabatic tranformation beforehand. Note that the coordinates of points B and D in the $p - V$ plane need to be suitably adapted. Particularly, now the volume of B is simply $V_B = V_C$, while $V_D = V_A T_C / T_A$. Let us proceed in computing the energy exchanges of the cycle:

- **$A \to B$.** In this isothermic expansion, the work is computed by means of Eq.(15) as $\Delta W_{AB} = -Nk_B T_A \ln(V_B/V_A)$. Since $V_B = V_C > V_A$, we thus have

$$\Delta W_{AB} = -Nk_B T_A \ln\left(\frac{V_C}{V_A}\right) < 0 \ . \tag{47}$$

  where the minus sign indicates that the work is being done by the system. Since the transformation is isothermic, one has $T_B = T_A$, so that there is no change in internal energy:

$$\Delta E_{AB} = (3/2)Nk_B(T_B - T_A) = 0 \ . \tag{48}$$

  Finally, the heat exchanged is computed from the first law as

$$\Delta Q_{AB} = -\Delta W_{AB} = Nk_B T_A \ln\left(\frac{V_C}{V_A}\right) > 0 \ . \tag{49}$$

  $\Delta Q_{AB} > 0$ implies that the system is absorbing heat.

- **$B \to C$.** In an isochore transformation, there is no work performed by or onto the system:

$$\Delta W_{BC} = 0 \ . \tag{50}$$

  The change in internal energy is $\Delta E_{BC} = (3/2)Nk_B(T_C - T_B)$. Since $T_B = T_A > T_C$, we get

$$\Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 \ . \tag{51}$$

  Hence, the system is cooling during BC. From the first law, we also have

$$\Delta Q_{BC} = \Delta E_{BC} = -\frac{3}{2}Nk_B(T_A - T_C) < 0 \ , \tag{52}$$

  so that in this step the system is releasing heat, as expected.

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- **$C \to D$.** This is another reversible isothermic transformation. The work is

$$\Delta W_{CD} = Nk_B T_C \ln\left(\frac{V_C}{V_D}\right) = Nk_B T_C \ln\left(\frac{V_C}{V_A}\frac{T_A}{T_C}\right) > 0 \tag{53}$$

while the heat echanged is (since $\Delta E_{CD} = 0$)

$$\Delta Q_{CD} = -\Delta W_{CD} = -Nk_B T_C \ln\left(\frac{V_C}{V_A}\frac{T_A}{T_C}\right) < 0 \ . \tag{54}$$

- **$D \to A$.** In this irreversible isobaric transformation, the work is

$$\Delta W_{DA} = -p_A(V_A - V_D) = -Nk_B(T_A - T_C) \ . \tag{55}$$

The change in internal energy is $\Delta E_{DA} = (3/2)Nk_B(T_A - T_C)$, so that the heat absorbed is

$$\Delta Q_{DA} = \Delta E_{DA} - \Delta W_{DA} = \frac{5}{2}Nk_B(T_A - T_C) \ . \tag{56}$$

The total work performed by the system is now obtained as usual, yielding

$$\Delta W = -Nk_B(T_A - T_C)\ln\left(1 + \frac{V_C}{V_A}\right) + Nk_B T_C \ln\frac{T_A}{T_C} < 0 \ . \tag{57}$$

Quantitatively, it corresponds again with the area enclosed by the cycle. However, *this is not true in general when irreversible transformations are involved.* In the present case, it is just due to the fact that the irreversible steps were isochore and isobaric transformations, where the work done is the same as in the reversible case. As for the heat adsorbed, we have $\Delta Q_a = \Delta Q_{AB} + \Delta Q_{DA}$, that is

$$\Delta Q_a = \frac{5}{2}Nk_B(T_A - T_C) + Nk_B T_A \ln\frac{V_C}{V_A} \ . \tag{58}$$

Note that, as mentioned above, the step DA is realized in practice by putting the system directly in contact with the hot source, so that the heat in this step is being adsorbed from this source. Hence, only two sources are present in this cycle, as in the case of the standard Carnot cycle. The efficiency thus reads

$$\eta = \frac{Nk_B(T_A - T_C)\ln\left(1 + \frac{V_C}{V_A}\right) - Nk_B T_C \ln\frac{T_A}{T_C}}{\frac{5}{2}Nk_B(T_A - T_C) + Nk_B T_A \ln\frac{V_C}{V_A}} \ . \tag{59}$$

As in the case of the Stirling and Carnot cycles, here we are considering a system working between two sources at temperatures $T_A > T_C$. In both of the previous cases, we obtained for the efficiency $1 - T_C/T_A$, so that a natural question is now whether this formula holds also in

the present case. To answer this question, we will consider the difference $\delta\eta \equiv (1 - T_C/T_A) - \eta$. Let us introduce also the ratio $q \equiv T_A/T_C > 1$. Starting from Eq.(59), we can write

$$\eta = \frac{-\ln q + (q-1)(1 + \ln \frac{V_C}{V_A})}{\frac{5}{2}(q-1) + q \ln \frac{V_C}{V_A}} \; . \tag{60}$$

Moreover, we note that $1 - T_C/T_A = (q-1)/q$. Hence, the difference $\delta\eta$ reads

$$\delta\eta = \frac{q-1}{q} - \frac{-\ln q + (q-1)(1 + \ln \frac{V_C}{V_A})}{\frac{5}{2}(q-1) + q \ln \frac{V_C}{V_A}} \; . \tag{61}$$

This can be manipulated to yield

$$\delta\eta = \frac{\frac{5}{2}(q-1) + q \ln \frac{V_C}{V_A} + \frac{q}{q-1}\ln q - q\left(1 + \ln \frac{V_C}{V_A}\right)}{q\left[\frac{5}{2}(q-1) + q \ln \frac{V_C}{V_A}\right]} = \frac{\frac{3}{2}q - \frac{5}{2} + \frac{q}{q-1}\ln q}{q\left[\frac{5}{2}(q-1) + q \ln \frac{V_C}{V_A}\right]} \; . \tag{62}$$

The denominator of the previous formula is evidently positive, since $q > 1$ and $V_C > V_A$. By taking the derivative with respect to q and checking its sign, it can be shown that the the numerator is an increasing function of q, so that its minimum value is found for the limiting case $q \to 1$. By considering this limit, one has $\ln q/(q-1) \to 1$, so that for $q \to 1$ one has $\delta\eta \to 0$. Nevertheless, this is a limiting case, and for $q > 1$ we find $\delta\eta > 0$, that is

$$\eta < 1 - \frac{T_C}{T_A} \; . \tag{63}$$

Therefore, *for the present case the cycle is less efficient than in the two reversible cases reported above.* Again, this is not a coincidence, but a consequence of the second law of thermodynamics by means of Carnot's theorem, as we discuss in the next section.

7 Quantitative formulation of the second law of thermodynamics

At the beginning of this document, we formulated the second law of thermodynamics in a qualitative way, following the Clausis formulation. Our aim is now to put it on a quantitative background.

7.1 Carnot's Theorem

The first step is provided by *Carnot's theorem: any reversible cycle which, as a net effect, involves heat exchange between the system and only two sources at temperatures $T_{hot} > T_{cold}$, has an efficiency equal to $\eta_{rev} = 1 - T_{cold}/T_{hot}$. Any irreversible cycle working under the same conditions has an efficiency lower than η_{rev}. Therefore, it also states that η_{rev} is the maximum efficiency that can be obtained by a machine working between these two sources.*

The examples treated above are some specific instances of this general theorem. Particularly, both the Carnot and Stirling cycles are reversible and involve only two sources (as a net effect), and their efficiency is indeed equal to $\eta_{\rm rev}$. In contrast, for the irreversible cycle considered in the right panel of Fig.11, we found $\eta < \eta_{\rm rev}$. In order to prove this theorem, let us consider a Carnot cycle C_c, which overall absorbs a heat $\Delta Q_{{\rm hot},C} > 0$ from $T_{\rm hot}$, produces a work $\Delta W < 0$ and releases a heat $\Delta Q_{{\rm cold},C} < 0$ to the source $T_{\rm cold}$. From the first law, $\Delta W + \Delta Q_{{\rm hot},C} + \Delta Q_{{\rm cold},C} = 0$. Moreover, we know that for this machine $\eta_C = -\Delta W/\Delta Q_{{\rm hot},C} = \eta_{\rm rev}$. Let us consider a second thermodynamic cycle X_c working between the same two sources and producing the same amount of work ΔW. The cycle absorbs $\Delta Q_{{\rm hot},X}$ from the hot source and releases $\Delta Q_{{\rm cold},X}$ to the cold source. The efficiency of this cycle is $\eta_X = -\Delta W/\Delta Q_{{\rm hot},X}$. As a next step, we imagine to build an engine which exploits the work produced by X_c to pump energy into a reversed Carnot cycle, which thus absorbs $-\Delta Q_{{\rm cold},C} > 0$ from the cold source and releases $-\Delta Q_{{\rm hot},C} < 0$ into the hot source. The combined machine does not produce work, while its heat exchanges are $\Delta Q_{\rm hot} = \Delta Q_{{\rm hot},X} - \Delta Q_{{\rm hot},C}$ with the hot source and $\Delta Q_{\rm cold} = \Delta Q_{{\rm cold},X} - \Delta Q_{{\rm cold},C}$ with the cold source.

Now, Carnot's theorem claims that $\eta_{\rm rev}$ is the largest efficiency that can be achieved. We proceed by a *reductio ad absurdum*, i.e. we hypothesize that the claim is false and see that it leads to a contradiction. Particularly, let us assume the the cycle X_c has an efficiency $\eta_X > \eta_C$. According to this hypothesis, we thus have $-\Delta W/\Delta Q_{{\rm hot},X} > -\Delta W/\Delta Q_{{\rm hot},C}$, i.e. $\Delta Q_{{\rm hot},X} < \Delta Q_{{\rm hot},C}$. Hence, we conclude that $\Delta Q_{\rm hot} < 0$, i.e. as a net effect the engine is releasing heat into the hot source. Since the overall work is zero (as well as the change in internal energy), we thus have that $\Delta Q_{\rm cold} = -\Delta Q_{\rm hot} > 0$ i.e. the engine is absorbing heat from the cold source. To sum up, we have thus built an engine which does not produce or need work and has as sole result the transfer of heat from a cold source to a heat source. This is in contrast with the second law of thermodynamics, so that our initial hypothesis was not correct. We thus conclude that $\eta_X \leq \eta_{\rm rev}$.

In the particular case in which X_c is also reversible, we can built the engine in the opposite way: a standard Carnot cycle produces work that is transferred to an inverted X_c in order to pump heat from the cold into the hot source. Proceeding in the same way as above, one demonstrates that $\eta_X \geq \eta_{\text{rev}}$. Therefore, for a reversible cycle the only option is that $\eta_X = \eta_{\text{rev}}$, which completes the proof.

7.2 Clausius' Theorem and the definition of Entropy

According to Carnot's theorem, for any cycle working between the two temperatures $T_{\text{hot}} > T_{\text{cold}}$, the efficiency η satisfies $\eta \leq 1 - T_{\text{cold}}/T_{\text{hot}}$. Now, let us consider a standard cycle, which absorbs heat $\Delta Q_{\text{hot}} > 0$ from the hot source and releases heat $\Delta Q_{\text{cold}} < 0$ into the cold source, producing a work $\Delta W = -(\Delta Q_{\text{hot}} + \Delta Q_{\text{cold}}) < 0$. Starting from the definition of η, Carnot's theorem implies $1 - T_{\text{cold}}/T_{\text{hot}} \geq -\Delta W/\Delta Q_{\text{hot}} = 1 + \Delta Q_{\text{cold}}/\Delta Q_{\text{hot}}$. Rearranging, this yields

$$\frac{\Delta Q_{\text{hot}}}{T_{\text{hot}}} + \frac{\Delta Q_{\text{cold}}}{T_{\text{cold}}} \leq 0 \ , \tag{64}$$

with the equality standing in the case of reversible machines.

Clausius' theorem extends this formula to an arbitrary number n of heat sources:

$$\sum_{i=1}^{n} \frac{\Delta Q_i}{T_i} \leq 0 \ , \tag{65}$$

where ΔQ_i is the heat exchanged with the source at temperature T_i. Particularly, this theorem holds for each infinitesimal transformation along the cycle, which gives at the continuum limit

$$\oint \frac{đQ}{T} \leq 0 \ . \tag{66}$$

where $\oint$ stands for a contour integral along the cycle. For the infinitesimal heat we are using the symbol $đQ$ rather than dQ to remember that it is an inexact differential, i.e. there is not a state variable Q. In the case of a reversible cycle, Eq.(66) becomes $\oint đQ/T = 0$. When a cycle integral of a differential is equal to 0, the differential itself comes from a state variable: we can thus define $dS \equiv (đQ/T)_{\text{rev}}$ as an exact differential, for which $\oint dS = 0$ as expected from a state variable. In the previous formula, the label $_{\text{rev}}$ serves to remind us that this calculation only stands for reversible cycles. The state variable S is called the *entropy* of the system and is defined up to an arbitrary additive constant.

Given two thermodynamic states A and B, their difference in entropy ΔS_{AB} depends only on the two states, i.e. it is independent of the transformation considered, since S is a state variable. However, for its practical calculation one has to consider an arbitrary *reversible* transformation from A to B and compute the entropy difference from the definition:

$$\Delta S_{AB} = \int_A^B \left(\frac{đQ}{T}\right)_{\text{rev}} \ . \tag{67}$$

Now, let us consider an arbitrary (reversible or irreversible) transformation $A \to B$. We consider it in conjunction with a reversible transformation $B \to A$, so that the combination is a cycle starting and ending in A. According to Clausius' theorem, we have $0 \geq \oint dQ/T = \int_A^B dQ/T + \int_B^A dQ/T = \int_A^B dQ/T + \Delta S_{BA} = \int_A^B dQ/T - \Delta S_{AB}$. Hence, for any transformation we get $\Delta S_{AB} \geq \int_A^B dQ/T$, where the equality holds for a reversible transformation. For an arbitrary infinitesimal transformation, we thus have $dS \geq dQ/T$. In the case of an isolated system, for which the transformation is adiabatic, one has $dQ = 0$, so that

$$dS \geq 0 \text{ for an isolated system.} \tag{68}$$

This is *the quantitative formulation of the second law of thermodynamics.*

The entropy gives also a clarification on the concept of irreversibility. Indeed, since the Universe is an isolated system, for any transformation its entropy can increase or remain constant, but never decrease. Therefore, an irreversible transformation for which $dS > 0$ cannot be reverted, since its reverse transformation would yield $dS < 0$, which is not allowed.

7.3 Some examples of entropy calculation

Let us consider some practical examples of entropy calculations. We consider a monoatomic ideal gas containing N molecules, for which we want to calculate the entropy variation ΔS_{AB} when passing from state A to state B. Let us assume that $V_A < V_B$. Since the entropy is a state variable, ΔS_{AB} does not depend on the particular transformation considered. However, its computation involves an arbitrary *reversible* function. It is instructive to consider various approaches.

In the first approach, in order to compute ΔS_{AB} we consider a combination of two transformations $A \to A'$ and $A' \to B$. The transformation $A \to A'$ is an adiabatic expansion to A', which we choose to have the same volume as B, $V_{A'} = V_B$. During this expansion, there is no heat exchange between the system and the environment, $\Delta Q_{AA'} = 0$. Therefore, there is no entropy change in this case: $\Delta S_{AA'} = 0$. From Eq.(17), the new temperature is $T_{A'} = T_A(V_B/V_A)^{2/3}$. Then, we consider for $A' \to B$ an isochore transformation. This reversible transformation is achieved by considering an infinite set of sources with temperatures ranging between $T_{A'}$ and T_B. The heat exchanged with one such source at temperature T is computed by considering the infinitesimal form of Eq.(13), yielding $dQ = (3/2)Nk_B dT$ independently of T. Hence, the computation of the entropy for this step is

$$\Delta S_{A'B} = \int_{A'}^B \frac{dQ}{T} = \frac{3}{2}Nk_B \int_{T_{A'}}^{T_B} \frac{dT}{T} = \frac{3}{2}Nk_B \ln \frac{T_B}{T_{A'}} = \frac{3}{2}Nk_B \ln \left[\frac{T_B}{T_A} \left(\frac{V_A}{V_B} \right)^{\frac{2}{3}} \right]. \tag{69}$$

The final value of the entropy change is $\Delta S_{AB} = \Delta S_{AA'} + \Delta S_{A'B} = \Delta S_{A'B}$, that is

$$\Delta S_{AB} = \frac{3}{2}Nk_B \ln \left[\frac{T_B}{T_A} \left(\frac{V_A}{V_B} \right)^{\frac{2}{3}} \right] = \frac{3}{2}Nk_B \ln \frac{T_B}{T_A} + Nk_B \ln \frac{V_A}{V_B}. \tag{70}$$

In the second approach, we consider again two transformations. However, $A \to A'$ is now an isothermic expansion, hence $T_{A'} = T_A$ (we still choose A' such that $V_{A'} = V_B$). In this case, from the first law $\Delta Q_{AA'} = -\Delta W_{AA'}$. From Eq.(15), we have that $\Delta Q_{AA'} = -\Delta W_{AA'} = Nk_B T_A \ln(V_B/V_A)$. The corresponding change in entropy is easily computed as

$$\Delta S_{AA'} = \int_A^{A'} \frac{đQ}{T} = \frac{1}{T_A} \int_A^{A'} đQ = \frac{\Delta Q_{AA'}}{T_A} = Nk_B \ln \frac{V_B}{V_A} \ . \tag{71}$$

The second transformation is again an isochore, so that the same results (suitably adapted) as above hold:

$$\Delta S_{A'B} = \int_{A'}^{B} \frac{đQ}{T} = \frac{3}{2} Nk_B \int_{T_{A'}}^{T_B} \frac{dT}{T} = \frac{3}{2} Nk_B \ln \frac{T_B}{T_{A'}} = \frac{3}{2} Nk_B \ln \frac{T_B}{T_A} \ . \tag{72}$$

The total change in entropy is thus

$$\Delta S_{AB} = \Delta S_{AA'} + \Delta S_{A'B} = Nk_B \ln \frac{V_B}{V_A} + \frac{3}{2} Nk_B \ln \frac{T_B}{T_A} \ , \tag{73}$$

which is the same result as above.

What about the entropy change of the surrounding environment? Since the system is assumed to be only a negligible perturbation in the environment, we can assume that whatever transformation we consider on the system, from the point of view of the environment it is slow enough to be always considered reversible. Considering the first scenario, since $A \to A'$ is adiabatic there is no heat exchange with the environment, whose entropy is thus untouched: $\Delta S_{AA'}^{\mathrm{env}} = 0$. In the reversible isochore transformation, each one of the infinite sources considered exchanges a heat with the system equal to $đQ^{\mathrm{env}} = -đQ = -(3/2)Nk_B dT$, hence it experiences a change in entropy equal to $dS^{\mathrm{env}} = đQ^{\mathrm{env}}/T$. The total change in entropy in the environment due to this transformation is given by the integral of all these infinitesimal contributions. It is easy to find that $\Delta S_{A'B}^{\mathrm{env}} = -\Delta S_{A'B}$. Hence, as a final result, for this set of transformations $\Delta S_{AB}^{\mathrm{env}} = -\Delta S_{AB}$. The total change of entropy in the universe (system plus environment) is thus $\Delta S_u = \Delta S_{AB} + \Delta S_{AB}^{\mathrm{env}} = 0$. It is straightforward to show that also in the second case we obtain the same result. This is expected, since for a set of reversible transformations $\Delta S = 0$ for an isolated system.

Now, what happens instead if one of the steps is irreversible? For instance, in the second scenario one could perform the isochore transformation directly by putting the system in contact with the source at temperature T_B. The change in entropy of the system is still the same, since it has to be calculated along a reversible transformation. In order to compute the change in entropy of the environment, as mentioned above we consider this transformation still as reversible. We focus only on the isochore transformation, since for the isothermic one the result is the same as above ($\Delta S_{AA'}^{\mathrm{env}} = \Delta S_{AA'}$). The heat exchanged with the system is $\Delta Q_{A'A}^{\mathrm{env}} = -\Delta Q_{A'A} = -(3/2)Nk_B(T_B - T_A') = -(3/2)Nk_B(T_B - T_A)$. From the point of view of the source,

this is a reversible transformation at constant temperature T_B, thus

$$\Delta S^{\text{env}}_{A'A} = \int_{A'}^{A} \frac{dQ}{T} = \frac{1}{T_B} \int_{A'}^{A} dQ = \frac{\Delta Q^{\text{env}}_{A'A}}{T_B} = -\frac{3}{2} N k_B \frac{T_B - T_A}{T_B} \ . \tag{74}$$

This is evidently different than before. The total change in entropy in the universe in this set of transformations is thus

$$\Delta S_u = \Delta S_{A'A} + \Delta S^{\text{env}}_{A'A} = \frac{3}{2} N k_B \ln \frac{T_B}{T_A} - \frac{3}{2} N k_B \frac{T_B - T_A}{T_B} \ . \tag{75}$$

By denoting $T_A/T_B \equiv q$, we can write $\Delta S_u = -\ln q - 1 + q$. It can be easily shown that the right-hand side is a function whose absolute minimum is obtained for $q = 1$. Hence, we have that $\Delta S_u > 0$ for $q \neq 1$. This is a particular instance of what mentioned above: whenever there is an irreversible process involved, the entropy of an isolated system (in this case, the universe) increases. In the present example, while it is possible to revert the state of the original system to state A (so that its overall entropy change is zero), the environment cannot be put in the same state as before, due to the positive change in entropy caused by the irreversible transformation. We note that in the special case $q = 1$ one has $\Delta S_u = 0$: this is because in this case $T_A = T_B$, i.e. there is no need to perform the isochore transformation.

8 Thermodynamic potentials

8.1 General observations

Thermodynamic potentials are state variables with the units of energy that provide powerful tools to determine the equilibrium conditions of a system. As we show below, they are always obtained by combining one extensive and one intensive quantity, whose product has the units of energy. Particularly, here we find the couples (p, V) and (T, S). These couples are known as *conjugate variables*. Note that in the case of matter exchange, one has also (μ, N). Moreover, other conjugate variables may be present depending on the particular system considered, e.g. for a polymer under tension one has $(\boldsymbol{f}, \boldsymbol{R}_e)$, where $\boldsymbol{f}$ is the force applied and $\boldsymbol{R}_e$ the vector joining the two ends. Depending on the context, other possibilities are for instance $(\boldsymbol{P}, \boldsymbol{E})$ in charged systems, where $\boldsymbol{E}$ is the applied electric field and $\boldsymbol{P}$ the electric polarization; for multiphasic systems, one can also have interface terms involving (σ, A), where σ is the surface tension and A the extension of the interface.

8.2 Helmholtz Free Energy

For an infinitesimal transformation, the first law of thermodynamics reads

$$dE = đQ + đW \ . \tag{76}$$

However, from the second law, we also have $đQ \leq T dS$, where the equality holds for reversible processes. Assuming that the infinitesimal work can be written as $đW = -p \, dV$, we can rephrase the first law as

$$đQ = dE + p \, dV \leq T dS \Rightarrow dE + p \, dV - T dS \leq 0 \ . \tag{77}$$

We define the *Helmholtz free energy* as

$$F = E - TS \ . \tag{78}$$

Since it is defined by means of state variables, F is itself a state variable. For any isothermic infinitesimal transformation, we can write

$$dF = dE - T dS \ . \tag{79}$$

From Eq. (77), we can thus write $đW = -p \, dV \geq dF$. This implies that in order to be able to extract work from a system ($đW < 0$), it is necessary to consider a transformation leading to a decrease in F. (indeed, if $dF > 0$ one gets $đW > 0$). For a given choice of initial and final states, the maximum work that can be extracted corresponds to the reversible transformation and is equal to dF. Hence, *the Helmholtz free energy corresponds to the maximum amount of work that can be extracted from a system under isothermic transformations.* Historically, it is this property that led to the introduction of the term "free energy".

Now, let us consider an infinitesimal transformation which is both isochore and isothermic. From the equation of state, this implies that the initial and final state are the same. However, if the transformation is irreversible the energy exchange follows the inequalities prescribed by the second law. From Eq.(77), we get $dF = dE - TdS \leq 0$ ($dV = 0$ since the transformation is isochore). Hence, *under isothermic and isochore conditions, the equilibrium state corresponds to the miminum Helmholtz free energy.*

Hence, at constant volume and temperature the Helmoltz free energy plays the role of the energy in "standard" mechanical systems. Now, from Eq.(77), we can write for a reversible infinitesimal transformation that

$$dE = -pdV + TdS \ . \tag{80}$$

Hence, the differential of F can be written as $dF = d(E - TS) = dE - SdT - TdS = -pdV + TdS - SdT - TdS = -pdV - SdT$. We thus get:

$$dF = -pdV - SdT \ , \tag{81}$$

which stresses that V and T are the relevant variables when dealing with F, which has a stationary point when they are constant.

From Eq.(81), we obtain

$$\left(\frac{\partial F}{\partial V} \right)_{N,T} = -p \qquad \left(\frac{\partial F}{\partial T} \right)_{N,p} = -S \ , \tag{82}$$

which are formulas connecting two conjugate variables by means of a derivative of a thermo-dynamic potential, known as *Maxwell relations*.

8.3   Gibbs Free Energy

We define the *Gibbs free energy* as

$$G = E - TS + pV = F + pV \ . \tag{83}$$

Again, this is a combination of state variables, so that G is a state variable. If we consider a transformation under constant pressure and temperature, from Eq.(77) we can write $dG = dE - TdS + pdV \leq 0$. Hence, *under isothermic and isobaric conditions, the equilibrium state corresponds to the miminum Gibbs free energy.*

This feature enables obtaining the equation of state of an ideal gas from the knowledge of its entropy and internal energy. Indeed, considering p and T as the independent variables, the equation of state defines the function $V = V(p, T)$. Under isothermic conditions, we know from Eq.(73) that $S = Nk_B \ln(V/V_0)$, where V_0 (for which $S = 0$) is an arbitrary reference volume

introduced to adimensionalize the argument of the logarithm. Moreover, for an ideal gas E depends only on its temperature. Minimization of G with respect to the volume yields:

$$\left(\frac{\partial G}{\partial V}\right)_{p,T} = p - \frac{Nk_BT}{V} = 0 , \tag{84}$$

from which the equation of state $pV = Nk_BT$ is recovered.

As for the Helmholtz free energy, also in the present case we can consider an infinitesimal reversible transformation. In this case we obtain $dG = d(F+pV) = -pdV - SdT + Vdp + pdV$, where we used Eq.(81). Hence, we find

$$dG = -SdT + Vdp , \tag{85}$$

which underlines that G is the relevant free energy when the control variables are T and p.

From the previous formula, we obtain the Maxwell relations for the Gibbs' free energy:

$$\left(\frac{\partial G}{\partial T}\right)_{N,p} = -S \qquad \left(\frac{\partial G}{\partial p}\right)_{N,T} = V . \tag{86}$$

8.4 Enthalpy

We define the *enthalpy* as

$$H = E + pV = G + TS . \tag{87}$$

Again, this is a combination of state variables, so that H is a state variable. If we consider a transformation under constant pressure and entropy, from Eq.(77) we obtain $dH = dE + pdV \leq 0$. Hence, *under isoentropic and isobaric conditions, the equilibrium state corresponds to the miminum enthalpy.* We note that for isobaric transformations dH represents the amount of heat exchanged. This is particularly useful for the study of chemical reactions and phase transitions, which usually happen at constant p.

For infinitesimal, reversible transformations, we get $dH = d(G + TS) = -SdT + Vdp + SdT + TdS$, where we used Eq. (85). We thus find:

$$dH = Vdp + TdS , \tag{88}$$

which underlines that H is the relevant thermodyncamic potential when the control variables are p and S.

From the previous formula, we obtain the Maxwell relations for the enthalpy:

$$\left(\frac{\partial H}{\partial p}\right)_{N,S} = V \qquad \left(\frac{\partial H}{\partial S}\right)_{N,p} = T . \tag{89}$$

8.5 Internal Energy

We observe that also the internal energy E is a thermodynamic potential, which is minimized under constant volume and entropy. We rewrite here the differential form of the first law

$$dE = -pdV + TdS , \qquad (90)$$

which underlines that E is the relevant thermodynamic potential when the control variables are V and S.

From the previous formula, we obtain the Maxwell relations for the internal energy:

$$\left(\frac{\partial E}{\partial V}\right)_{N,S} = -p \qquad \left(\frac{\partial E}{\partial S}\right)_{N,V} = T . \qquad (91)$$

Finally, we also mention the existence of the so-called *grand potential* Ω, which is employed when there is also matter exchange (i.e. N is not a constant).

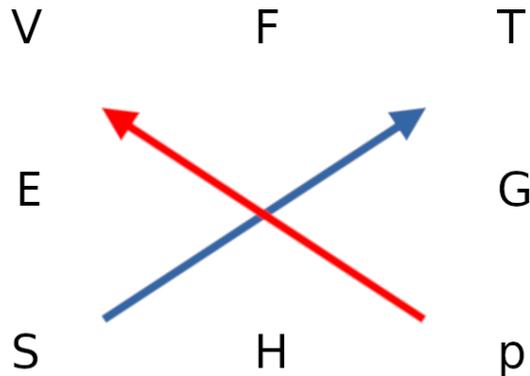## 8.6 Maxwell Relations and thermodynamic forces

Figure 12: Schematic summary of Maxwell relations (from K. Huang, "Statistical Mechanics").

In Fig.12, we report a schematic drawing which summarizes the eight Maxwell relations, Eq.(82), Eq.(86), Eq.(89) and Eq.(91). In the scheme, each thermodynamic potential is flanked by the corresponding independent variables to be considered. The derivative corresponding to a given variable is found by following the arrow and assigning a plus or a minus sign according to whether the arrow is followed in the forward or backward direction.

The Maxwell relations give the response of a thermodynamic potential to the change in one of the control variables. In this regard, they are akin to force in mechanical systems, which is obtained as the derivative of the potential energy with respect to position. For instance, we know that for a one-dimensional spring the potential energy E_s is $E_s(x) = \frac{1}{2}k_m x^2$, where k_m is the spring constant. If we displace the spring from its equilibrium position, we obtain an

elastic response via the force $f = -dE_s/dx = -k_m x$. The Maxwell relations are analogous to this example, so that one can look at the conjugate variables as generalized displacement and forces. For the latter, the term *thermodynamic forces* is often employed. For instance, if the control variables are T and V, we know that the right thermodynamic potential to consider is the Helmholtz free energy. We can regard the volume as a generalized coordinate and, from Eq.(82), look at $p = -(\partial F/\partial V)_{N,T}$ as the corresponding generalized force. Going back to the spring analogy, we note that k_m quantifies how strong is the response for a given displacement, which in the thermodynamic context is known as the *susceptibility* of the system. Mathematically, it is related to the potential energy as $k_m = d^2 E_s/dx^2$. In a thermodynamic system at constant T and V, we can define in a similar way a susceptibility relative to changes in volume (the *isothermic compressibility k_β*) as $(\partial^2 F/\partial V^2)_{N,T} = -(\partial p/\partial V)_{N,T} \equiv k_\beta/V$. Note that in the definition we divide by V in order for k_β to be intensive.

Problem. Show that for an ideal gas one has $k_\beta = p$.

Further reading

- L. E. Reichl, *A Modern Course in Statistical Physics*, 4th Edition, Chapter 3, Wiley-VCH

- K. Huang, *Statistical Mechanics*, 2nd Edition, Chapter 1, John Wiley & Sons

- P. Mazzoldi, M. Nigro and C. Voci, *Fisica - Volume I* (in Italian), 2nd Edition, Chapters 11-13

- R. Delgado Buscalioni, notes on Thermodynamics (you can find them in the Moodle)