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Thermostatics

The goal of this first chapter is to give a presentation of thermodynamics, due to H. Callen, which will allow us to make the most direct connection with the statistical approach of the following chapter. Instead of introducing entropy by starting with the second law, for example with the Kelvin statement 'there exists no transformation whose sole effect is to extract a quantity of heat from a reservoir and convert it entirely to work', Callen assumes, in principle, the existence of an entropy function and its fundamental property: the principle of maximum entropy. Such a presentation leads to a concise discussion of the foundations of thermodynamics (at the cost of some abstraction) and has the advantage of allowing direct comparison with the statistical entropy that we shall introduce in Chapter 2. Clearly, it is not possible in one chapter to give an exhaustive account of thermodynamics; the reader is, instead, referred to classic books on the subject for further details.

1.1 Thermodynamic equilibrium

1.1.1 Microscopic and macroscopic descriptions

The aim of statistical thermodynamics is to describe the behaviour of macroscopic systems containing of the order of $N \approx 10^{23}$ particles.[1] An example of such a macroscopic system is a mole of gas in a container under standard conditions of temperature and pressure.[2] This gas has 6×10^{23} molecules[3] in incessant motion, continually colliding with each other and with the walls of the container. To a first approximation, which will be justified in Chapter 2, we may consider these molecules as classical objects. One can, therefore, ask the usual question of classical mechanics: given the initial positions and velocities (or momenta) of the

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[1] With some precautions, one can apply thermodynamics to mesoscopic systems, i.e. intermediate between micro- and macroscopic, for example system size of the order of 1 μm.

[2] The reader will allow us to talk about temperature and pressure even though these concepts will not be defined until later. For the moment intuitive notions of these concepts are sufficient.

[3] In the case of a gas, we use the term 'molecules' instead of the generic term 'particles'.

molecules at $t = 0$, what will the subsequent evolution of this gas be as a function of time? Let us, for example, imagine that the initial density is non-uniform and ask how the gas will evolve to re-establish equilibrium where the density is uniform. Knowing the forces among the molecules and between molecules and walls, it should be possible to solve Newton's equations and follow the temporal evolution of the positions, $\vec{r}_i(t), i = 1, \ldots, N$, and momenta, $\vec{p}_i(t)$, as functions of the positions and momenta at $t = 0$. We could, therefore, deduce from the trajectories the evolution of the density $n(\vec{r}, t)$. Even though such a strategy is possible in principle, it is easy to see that it is bound to fail: if we simply wanted to print the initial coordinates, at the rate of one coordinate per microsecond, the time needed would be of the order of the age of the universe! As for the numerical solution of the equations of motion, it is far beyond the capabilities of the fastest computers we can imagine, even in the distant future. This kind of calculation, called molecular dynamics, can currently be performed for a maximum of a few million particles.

The quantum problem is even more hopeless: the solution of the Schrödinger equation is several orders of magnitude more complex than that of the corresponding classical problem. We keep in mind, however, that our system is, at least in principle, susceptible to a microscopic description: positions and momenta of particles in classical mechanics, their wave function in the quantum case. If this information is available, we will say that a system has been attributed a *microscopic configuration* or *microstate*. In fact, this microscopic description is too detailed. For example, if we are interested, as above, in the temporal evolution of the density of the gas, $n(\vec{r}, t)$, we have to define this density by considering a small volume, ΔV, around the point $\vec{r}$, and count (at least in principle!) the average number of gas molecules in this volume during a time interval, Δt, centred at t. Even though ΔV is microscopic, say of the order of 1 μm on a side, the average number of molecules will be of the order of 10^7. We are only interested in the average number of molecules in ΔV, not in the individual motion of each molecule. In a macroscopic description, we need to make spatial and temporal averages over length and time scales that are much larger than typical microscopic scales. Length and time scales of 1 μm and 1 μs are to be compared with characteristic microscopic scales of 0.1 nm and 1 fs for an atom. In this averaging process, only a small number of combinations of microscopic coordinates will play a rôle, and not each of these coordinates individually. For example, we have seen that to calculate the density, $n(\vec{r}, t)$, we have to count all molecules found at time t in the volume ΔV around point $\vec{r}$, or, mathematically,

$$n(\vec{r}, t) = \frac{1}{\Delta V} \int_{\Delta V} \mathrm{d}^3 r \sum_{i=1}^{N} \delta\left(\vec{r} - \vec{r}_i(t)\right) \tag{1.1}$$

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This equation selects a particular combination of positions, $\vec{r}_i(t)$, and gives an example of what we will call *macroscopic variables*. Another example of a combination of microscopic coordinates yielding a macroscopic variable will be given below for the energy (Equation (1.2)).

Since the microscopic approach leads to a dead end, we change descriptions, and take as fundamental quantities global macroscopic variables related to the sample: number of molecules, energy, electric or magnetic dipole moment, etc. Macroscopic variables, or more precisely, their densities (density of molecules, of energy etc.) define a *macrostate*. The evolution of macroscopic variables is governed by deterministic equations: Newton's equations for elastic objects, Euler's equations for fluids, Maxwell's equations for electric or magnetic media, etc. However, this purely mechanical description is insufficient since a macrostate is compatible with a very large number of different microstates. Therefore, we cannot forget the microscopic degrees of freedom that have been eliminated by averaging. For these microscopic degrees of freedom, which, for the moment, we have ignored in the macroscopic approach, we will use a probabilistic description; this will in turn lead to the concept of entropy, which is needed to complete our macroscopic picture. This probabilistic approach will be discussed in Chapter 2. Contrary to other macroscopic variables, *entropy is not a combination of microscopic variables*: it plays a singular rôle compared to other macroscopic quantities.

In the remainder of this chapter, we will limit ourselves to a thermodynamic description and only consider macroscopic variables and the entropy.

1.1.2 Walls

A particularly important macroscopic variable in thermodynamics is the energy, which can take many forms. In a mechanical system with only conservative forces (derivable from a potential), the mechanical energy, which is the sum of the kinetic and potential energies, is conserved. A mechanical system protected from all external influences, i.e. *isolated*, finds its energy conserved, in other words independent of time. Mathematically, the energy can be written as

$$\boxed{E = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2} \sum_{i \neq j} U(\vec{r}_i - \vec{r}_j)} \tag{1.2}$$

To simplify the writing, we have assumed in this equation that the particles are identical and of mass m; $\vec{p}_i$ is the momentum of particle i, $\vec{r}_i$ its position, and U the potential energy of two molecules. We also assumed the molecules to have no internal structure. Equation (1.2) also gives the expression for the classical or quantum Hamiltonian, H, of the isolated system. In the quantum case, $\vec{p}_i$ and

$\vec{r}_i$ are the canonically conjugate momentum and position operators for particle i. When the system is not isolated, we know that we can transfer mechanical energy to it: when we compress a spring, it acquires additional energy, which it stores in the form of elastic potential energy. During the compression process, the point where the force is applied moves with the consequence that energy is given to the system in the form of *work*. Similarly, we supply energy to a gas by compressing it with the help of a piston. In both cases, the *external parameters*[4] of the system, length of the spring in one case, volume of the gas in the other, are modified in a known way. However, we know, experimentally, that we can transfer energy to an object in many other ways. Any handyman knows that we can transfer energy to a drill bit by drilling a hole in concrete. The bit heats up due to friction, and, according to a popular but thermodynamically incorrect statement (Footnote 10), some of the mechanical energy supplied by the drill motor is 'changed to *heat*'. We can obtain the same result by leaving the drill bit in the sun on a hot summer day, which corresponds to 'transforming electromagnetic energy into heat', or by immersing it in boiling water, i.e. by using thermal contact. In the latter case, there is no visible modification of external variables (see Section 2.5.1) either of the bit or of the water. Only the microscopic degrees of freedom are involved in the exchange of energy. The heating of the bit corresponds to bigger vibrations of its atoms around their equilibrium positions, the concomitant cooling of the water corresponds to a reduction of the average speed of its molecules.[5] *Energy transfer in the form of heat is characterized by the fact that neither the external parameters of the system, nor the configuration of the external medium, are modified*. This heat transfer can be effected by conduction (the drill bit in contact with water), or by radiation (between the sun and the bit).

In summary, a system can receive energy either in the form of work, or in the form of heat. The energy supplied in the form of work is, at least in principle, measurable from mechanical considerations because work is supplied by a macroscopic mechanical device whose parameters (masses, applied forces, etc.) are, supposedly, perfectly known.[6] Work is obtained by causing a change, either of the external parameters, or the configuration of the external medium, or both. However, the amount of energy received by an object is not known with precision from the principle of conservation of total energy unless we are able to eliminate energy exchange in the form of heat. This can be accomplished by isolating the system using a heat insulating wall, or an *adiabatic wall*; on the other hand, a *diathermic wall*

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[4] External parameters are those quantities that are under the direct control of the experimentalist: volume, external electric or magnetic fields, etc.

[5] To simplify the discussion, we neglect complications due to the potential energy of the molecules.

[6] From this point of view, the energy supplied by an electric device will be considered as work since it can be determined by electric measurements performed with a voltmeter or an ammeter.

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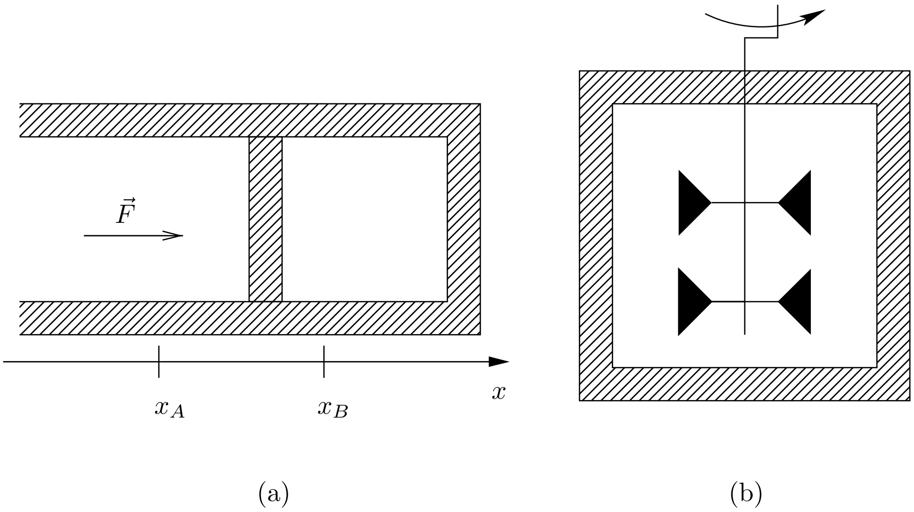

Figure 1.1 Two ways to supply work. (a) Compressing a gas, (b) Joule's experiment.

allows heat transfer. Inversely, we eliminate energy transfer in the form of work by using a *rigid wall* not penetrated by any mechanical device.[7] The possibility of a thermodynamic description is founded on the existence, at least in theory (since walls are never perfectly adiabatic or rigid!), of walls capable of controlling the different forms of energy transfer.

An *isolated system* is a system that cannot exchange energy with its surroundings in any form whatsoever: it is isolated from the external world by walls that are perfectly adiabatic, rigid, impermeable to molecules and shielded electrically and magnetically.

1.1.3 Work, heat, internal energy

We now develop more quantitatively the concepts defined above. First we need to make an essential distinction between two different ways of supplying work. To fix ideas, let us consider work done on a gas by compressing it with the help of a piston displaced between positions x_A and x_B (Figure 1.1(a)), the position of the piston being given by its abscissa x. If at every instant the position of the piston and $F(x)$, the component of the applied force parallel to Ox, are perfectly controlled,

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[7] Rigorously speaking, for a mechanical system one also should eliminate energy transfer by other processes such as electric or magnetic.

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the work $W_{A\to B}$ can be calculated by integrating between x_A and x_B the element of work $đW$

$$đW = F(x)\,\mathrm{d}x$$
$$W_{A\to B} = \int_{x_A}^{x_B} \mathrm{d}x\, F(x) \tag{1.3}$$

While compressing the gas, the external parameter, x, and the force, $F(x)$, are entirely under the control of the experimenter who performs a *quasi-static transformation*. This important notion will be defined in general in Section 1.2.2. An example where work transfer is *not* quasi-static is studied in Problem 1.7.1. A vertical cylinder containing gas is closed with a piston on which a weight is placed. When this weight is suddenly removed, the gas expands and the piston reaches a new equilibrium position after a few oscillations. Neglecting the friction between the piston and the cylinder, the work supplied to the gas is $-P_{\mathrm{ext}}\Delta V$, where P_{ext} is the external pressure and ΔV the change in volume. This change in volume was not controlled during the expansion of the gas. Another example of non-quasi-static transfer of work is illustrated in Figure 1.1(b). The system is isolated from the exterior by an adiabatic wall, but a motor turns vanes in the fluid, which heats up due to viscosity. The energy supplied in the form of work can be calculated from the characteristics of the motor.[8] These two examples of non-quasi-static work transfer appear very different but do have a point in common. In the first example, the final temperature is higher than it would have been had the change been quasi-static, and, as is the case in the second example, viscous forces are responsible for the increase in temperature. The example of the heated drill bit, given earlier, is another illustration of work done non-quasi-statically.

We now examine the energy transfer between states of a system. Let A and B be two possible arbitrary states. The energy of each of these states is, in principle, a well-defined quantity, for example by Equation (1.2). In thermodynamics, this is called the *internal energy* and will be denoted by E. We know that only energy differences have physical meaning, and that *a priori* the interesting quantity is $E_B - E_A$. Our goal is to demonstrate that this energy difference is accessible experimentally. Note that all transferred energies, be they in the form of work or heat, are algebraic quantities that can be positive or negative.

Taking E_A as the reference energy, we will be able to determine E_B if it is possible to go from A to B by supplying the system only with work, positive or

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[8] A more modern version of this experiment, which dates back to Joule, consists of putting in the fluid a known resistance across which we apply a known potential difference: the amount of electrical energy ‘transformed into heat’ is thus known.

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negative, since this work, furnished by a mechanical device, is measurable. To determine whether such a transformation is possible, we start from the following empirical observation. It is possible to go either from state A to state B, or from state B to state A by a process whose sole effect is to supply work to the system. However, under this condition, only one of the two transformations is allowed. We justify this statement as follows. If states A and B have the same volume, and if $E_B > E_A$, a mechanism similar to that in Figure 1.1(b) allows us to go from A to B, which will be impossible if $E_B < E_A$.[9] If the volumes of A and B are different, we can use an adiabatic expansion or compression, $A \to A'$, which brings the system to the desired volume, $V_{A'} = V_B$, with an energy $E_{A'}$. If $E_{A'} < E_B$, work can be done to arrive at the final state with energy E_B. To summarize, we can determine, either $E_B - E_A$ by a transformation $A \to B$, or $E_A - E_B$ by a transformation $B \to A$, by supplying only measurable work to the system.

If the transformation $A \to B$ is now performed in an arbitrary manner, in other words it involves an exchange of both work and heat, we can control the work, $W_{A\to B}$, which is determined by macroscopic mechanical parameters. The energy difference, $(E_B - E_A)$, has previously been determined, and we thus obtain the amount of heat, $Q_{A\to B}$, supplied in this process

$$\boxed{Q_{A\to B} = (E_B - E_A) - W_{A\to B}} \tag{1.4}$$

This equation, which simply expresses conservation of energy, constitutes the ‘first law of thermodynamics’. It is often written in the differential form

$$\boxed{đQ = \mathrm{d}E - đW} \tag{1.5}$$

Unlike the increase in the internal energy, $E_{A\to B} = E_B - E_A$, the work, $W_{A\to B}$ and the amount of heat, $Q_{A\to B}$, are not determined by the initial and final states: they depend on the transformation itself.[10] This is why, unlike the differential $\mathrm{d}E$, the infinitesimal quantities $đQ$ and $đW$ are not differentials. We can understand this intuitively by making an analogy with mechanics. If a force, $\vec{F}$, is such that $\vec{\nabla} \times \vec{F} \neq 0$, the work it does between points A and B

$$W_{A\to B} = \int_A^B \vec{F}\cdot \mathrm{d}\vec{l}$$

does not depend only on the points A and B. It also depends on the path taken, and there is no function whose differential gives the infinitesimal work.

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[9] Anticipating what is to follow, $E_B > E_A$ means that the temperature, T_B, of B is greater than T_A of A: it is impossible to cool down a volume simply by exchanging work.

[10] We cannot, therefore, ascribe to a system a work or heat content. The concepts of heat and work expose two different forms of *energy exchange* between two systems: heat and work are ‘energy in transit’.

1.1.4 Definition of thermal equilibrium

For simplicity, we limit ourselves to the ideal case of a system that is shielded from electric or magnetic influences, leaving these more complex cases to the references. This restriction is not a limitation of the theory, but merely a convenience to simplify the discussion. Suppose that our system is isolated in a completely arbitrary initial state, for example with a spatially dependent density. *Experience tells us that if we wait long enough, the system will evolve to an equilibrium state, that is a state which depends neither on time nor on the past history of the system.* The equilibrium state is entirely characterized by macroscopic variables and external parameters describing the system: the volume, V, the energy, E, and the numbers, $N^{(1)}, \ldots, N^{(r)}$, of molecules of type $1, \ldots, r$.

The time that characterizes the approach to equilibrium is called the *relaxation time*. Relaxation times can be as short as a few microseconds, and as long as several millennia. It is, therefore, not obvious in practice to decide whether or not we have attained an equilibrium state. In numerous cases, we only reach a state of metastable equilibrium whose average lifetime can be extremely long. Such a state only appears to be independent of time, and in fact also depends on its past history. A very familiar example is hysteresis: if we magnetize an initially unmagnetized sample of magnetic material by applying a magnetic field, the magnetization does not disappear when the field is removed. The evolution of the magnetization, M, as a function of the applied magnetic field, B, describes a hysteresis cycle as shown in Figure 1.2. On this figure, the dashed line represents the case where the initial magnetization is zero. The magnetic state, therefore, depends on its past history even though we have obtained a magnet that is apparently in a stable state. However, we may, for example, reach a state whose magnetization is opposite to the magnetic

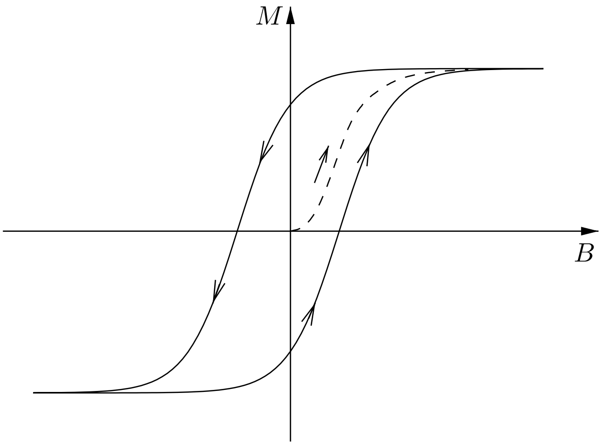

Figure 1.2 Hysteresis cycle for a magnetic system in an external field.

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field, a state that is clearly metastable. Another common case is the existence of a variety of metastable crystals: for example, graphite is the stable crystalline form of carbon under standard conditions of pressure and temperature, and diamond is metastable. There are many other examples: glasses, alloys, memory materials, etc. In such cases, if we mistakenly assume that the system is at equilibrium, we may arrive at conclusions that contradict experiment.

While keeping in mind the difficulty related to extremely long relaxation times, *we take as our first postulate the existence of equilibrium states*: an isolated system will attain, after sufficiently long time, an equilibrium state that is independent of its past history and characterized by its own intrinsic properties such as volume V, energy E and numbers $N^{(i)}$, of molecules of different types. In what follows, we shall often limit ourselves to a single type of molecule, N in number, and to homogeneous equilibrium states whose properties, for example the density, are uniform. The quantities E, V, and N are said to be *extensive*: if we merge into one system two identical subsystems at equilibrium, the energy, volume and number of molecules are doubled.

1.2 Postulate of maximum entropy

1.2.1 Internal constraints

As we have emphasized in the introduction, our presentation of thermodynamics postulates the existence of an entropy function. To define it correctly, it is necessary to introduce the notion of *internal constraint*, of which we shall give a simple example. Consider an isolated system that we have divided in two subsystems (1) and (2), separated by a piston (Figure 1.3). As always, we assume that the contributions of the walls (or the piston) to the energy, E, to the volume, V, and to the total number of molecules, N, are negligible since they arise from surface effects. Consequently, E, V, and N represent the sums of energies, volumes and

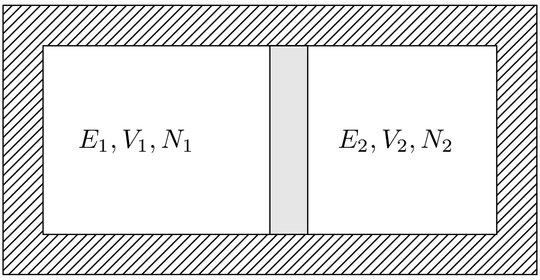

Figure 1.3 An isolated system which is divided into two ‘subsystems’.

numbers of particles in the two subsystems

$$E = E_1 + E_2 \qquad V = V_1 + V_2 \qquad N = N_1 + N_2 \tag{1.6}$$

The piston creates the following internal constraints:

- If it is fixed, it creates a constraint in preventing the free flow of energy from one subsystem to the other in the form of work.
- If it is adiabatic, it creates a constraint in preventing the free flow of energy from one subsystem to the other in the form of heat.
- If it is impermeable to molecules, it creates a constraint in preventing the flow of molecules from one subsystem to the other.

We lift a constraint by rendering the piston mobile, diathermic or permeable. We can, of course, lift more than one constraint at a time.

Let us start with the following initial situation: the piston is fixed, adiabatic, impermeable, and both subsystems are separately at equilibrium. We lift one (or several) of the constraints and we await the establishment of a new equilibrium state. We can then pose the following question: what can we say about this new equilibrium state? We shall see that the answer to this fundamental question is given by the principle of maximum entropy.

1.2.2 Principle of maximum entropy

We make the following postulates, which are equivalent to the usual statement of the ‘second law of thermodynamics’:

(*i*) *For any system at equilibrium, there exists a positive differentiable entropy function* $S(E, V, N^{(1)}, \ldots, N^{(r)})$.[11] *As a general rule, this function is an increasing function of* E *for fixed* V *and* $N^{(i)}$.[12]

(*ii*) *For a system made of* M *subsystems,* S *is additive, or extensive: the total entropy* S_{tot} *is the sum of the entropies of the subsystems,*

$$S_{\text{tot}} = \sum_{m=1}^{M} S(E_m, V_m, N_m^{(1)}, \ldots, N_m^{(r)}) \tag{1.7}$$

(*iii*) *Suppose the global isolated system is initially divided by internal constraints into subsystems that are separately at equilibrium: if we lift one (or more) constraint, the final entropy, after the re-establishment of equilibrium must be greater than or equal to the initial entropy. The new values of* $(E_m, V_m, N_m^{(i)})$ *are such that the entropy can only increase or stay unchanged. In summary: the entropy of an isolated system cannot decrease.*

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[11] The reader will remark that S is, at the same time, a function of an external parameter V, and macroscopic variables E and N.

[12] See Problem 3.8.2 for an exception.