From Dynamics to Thermodynamics

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Chapter 1

Lecture 1: a crash course in thermodynamics

In this first lecture we will recall some basic fact of classical thermodynamics. Thermodynamics is defined by some *given* principles or laws, and the object of the thermodynamics are those system that satisfy these laws. This is still quite vague. In fact thermodynamics describe certain possible transformation from one equilibrium to another, without precising the time scale (nor the space scale) where these changes happen. Later we will try to understand, starting from a microscopic dynamics, how we describe the equilibrium states of the system (this is the scope of equilibrium statistical mechanics) and at what space-time macroscopic scale we obtain the transformations described by the principles of thermodynamics. Mathematically space-time macroscopic scale means we will perform a scaling limit.

We will consider only the most simple system that contains the main ideas: a one dimensional bar, or elastic, whose equilibrium thermodynamic states are parametrized by the *tension* and the *temperature* (intensive parameters), or by the length and the energy (*extensive parameters*). This very simple model permits to avoid many complications (like phase transitions) and we will introduce only the minimal thermodynamic concept necessary. There exist many very good thermodynamic books were the general theory is developed. Still we keep this chapter self contained, sometime anticipating the connection with the statistical mechanics model we will develop in the following lectures.

The strategy is the following: we will state here the *Thermodynamic laws*, as kind of axioms and we will recover them later from mechanics (or more precisely we will indicate what mathematical theorems should be proven in order to recover them from mechanics.

1.1   The 0-law: Thermodynamic equilibrium states

From a mechanical point of view, the *equilibrium* state of an elastic wire is characterized by its *length* $\mathcal{L}$, that is a function of a *tension* (force) τ applied on the extremes. The resulting length is a function (usually increasing) of τ: $\mathcal{L} = \mathcal{L}(\tau)$. A way to apply the tension τ to the wire, is to attach one side of the wire to a fixed point, and apply the force τ to the other end. In our treatment we will consider $\tau \in \mathbb{R}$, and $\mathcal{L} \in \mathbb{R}$, i.e. can assume negatives values, typically if a negative tension τ is applied.

The length $\mathcal{L}$ depends also on the *temperature θ* of the wire. The first object of thermodynamics is to introduce this parameter θ, whose definition (or measurement) is much more delicate than $\mathcal{L}$ or $\boldsymbol{\tau}$.

Two wires can be connected together by attaching (*gluing*) one of the two extremities. Of course there are many other ways to put together two wires, but for our purpouses this would be enough.

The definition of temperature goes through first defining when two systems are at the same temperature, by what is called the *0th law of thermodynamics*[1]:

> *If a wire A, under the tension $\boldsymbol{\tau}$, remains in equilibrium when isolated and placed in <u>contact</u> first with the wire B and then with the wire C, both at the same tension $\boldsymbol{\tau}$, the equilibrium of B and C will not be disturbed when they are placed in contact with each other.*

It means that if A keeps the same length $\mathcal{L}_A$ when put in contact to the wire B and with the wire C, both under the same tension $\boldsymbol{\tau}$, then we say that B and C are at the same temperature, that will be the temperature of A.

From the zero law we obtain the existence of the parameter θ which we call *temperature*. Of course this parametrization is not unique and this is the reason we have different scales of temperatures (see in Zemansky [12] a very detailed discussion of this point). In fact by itself, without comparing with a real quantity (like the volume of a gas, or the high of the mercury level) it does not define the sign of θ.

Consequently we can define the equilibrium relation $\mathcal{L} = \mathcal{L}(\boldsymbol{\tau}, \theta)$, the detailed form of this function depends on the material which constitute the wire. Typically $\mathcal{L}(\boldsymbol{\tau}, \theta)$ is strictly monotone in both variables, so we can also write $\boldsymbol{\tau} = \boldsymbol{\tau}(\mathcal{L}, \theta)$, as

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[1]The numbering of the principles in thermodynamics follows an inverse chronological order: the second principle was postulated by Carnot in 1824, the first principle was clearly formulated by Helmholtz and Thomson (Lord Kelvin) in 1848, while the need of the zero principle was realized by Fowler in 1931. See the detailed discussion in the first chapter of Zemansky

well as $\theta = \theta(\mathcal{L}, \boldsymbol{\tau})$, i.e. any two of these three variables can be chosen independently in order to characterize a thermodynamic equilibrium state.

If we look at the 0-law from a dynamical point of view, this defines much more than the temperature. The 0-Law says that we know what all the equilibrium states of the system, that they are **all** parametrized by the tension and temperature, or by tension and volume etc. It means that, once fixed the temperature and the tension, there are no other equilibrium states depending on other quantities. We can also take an even stronger dynamical point of view: these equilibrium states are *stable*, than means if we change one of this external parameters, for example the tension, our system will reach one of these equilibrium states, after going through some non-equilibrium situations that we do not investigate here. We will see that this is connected to specific *ergodic* properties of the microscopic dynamics, in particular that there are only two *relevant conserved quantities* in the infinite dynamics are the elongation and the energy.

1.1.1   Heat bath or thermostats

If it is completely clear how to fix or change the tension in our system, we need the notion of *heat bath* in order to fix the temperature. Heat bath, or thermostat, should be a much bigger system in equilibrium at a given temperature, so much bigger that its equilibrium state remains unchanged if it is in *contact* with our wire. In the case that this contact is all along the bulk of the wire, we can think that the wire is immersed in a gaz or a fluid. We say that the temperature of the heat bath is θ if we immerge our wire in it with tension $\boldsymbol{\tau}$ and, when equilibrium is reached, the length of the wire is $\mathcal{L}(\boldsymbol{\tau}, \theta)$. We can also have these heat bath or thermostats acting only at one or more of the boundaries of our system.

Of course this is an idealization of a real heat bath, whose equilibrium would be changed at least locally by the contact with the wire, unless this is at the same temperature. But in an ideal heat bath there is no spacial structure, and the effect of the system on the bath is negligeable.

We consider this notion of heat bath as primary in the theory, like for the force $\boldsymbol{\tau}$: we are not interested in knowing who is pulling as long as the work is done correctly. So we are not interested here in the *mechanism* that keeps the temperature constant. When constructing the microscopic dynamics later, we will discuss stochastic dynamics that will work as ideal thermostats in a macroscopic limit.

When the system is in contact with such ideal thermostat, the 0-law says that it will reach an equilibrium with temperature equal to the one of the thermostat.

1.2   The 1st Law: Work, Internal Energy and Heat exchange

Adiabatic transformations, work and internal energy

Let us start with our wire in equilibrium at tension $\boldsymbol{\tau}_0$ and temperature θ_0. Keeping the wire isolated (no heat bath in contact) we change the tension to $\boldsymbol{\tau}_1$. The system will go out of equilibrium, waves will run through it, its length $\mathcal{L}$ will change in time. If the material of the wire has the right properties, we expect that, *after a long time*[2], the waves get dissipated and a new equilibrium is reached with tension $\boldsymbol{\tau}_1$. This is in fact the assumption made by the 0-law. A measure of the temperature of this new equilibrium state will result in general at a different value θ_1. We call **adiabatic** this transformation from an equilibrium to another for an isolated system (except for the tension $\boldsymbol{\tau}_1$ applied).

We will see that to obtain the existence of adiabatic transformations with these properties from the *microscopic* dynamics is one of the major problems of the theory. But the 0-Law, in the interpretation we gave in the previous section, assumes that these adiabatic transformations exist.

The work done by the external force $\boldsymbol{\tau}_1$ is already well defined by classical mechanics as $W_1 = \boldsymbol{\tau}_1(\mathcal{L}_1 - \mathcal{L}_0)$. Notice that this definition does not require any information about time scales, or about how the system reaches the new equilibrium. In the case we are applying a non-constant force $\tilde{\tau}(s)$, we need a more careful definition of work, as

$$W = \int_0^{t_1} \tilde{\tau}(s)d\mathcal{L}(s) \tag{1.2.1}$$

that requires the knowledge of $\mathcal{L}(t)$, the time evolution of the length of the wire[3].

Mechanics defines *energy* as a quantity associated to a state of the system that work modifies. It means that if on the system acts only the force τ_1 (or $\tilde{\tau}(\cdot)$), then the *energy* of the system U increase (or decrease) by the work W_1 (or W), i.e. in these adiabatic trasformations we have the change of the energy inside the system (internal energy) $\Delta U = W$.

In the notation used here, $W > 0$ means we are doing work on the system, increasing its internal energy; if $W < 0$ we are obtaining work from the system, decreasing the internal energy.

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[2]Thermodynamics is not concerned in the time scale at which systems reach equilibrium, or transformation take place.

[3]Notice that $\tilde{\tau}(s)$ in (1.2.1) is just the tension applied to the system at the right end side, and in general does not correspond to a value of the tension inside the wire.

Heat.

After the adiabatic trasformation described above, we have obtained the system at a new equilibrium that has tension τ_1, length $\mathcal{L}_1$ and temperature θ_1. We can also say that if U_0 was the initial energy, the system has now an energy equal to $U_1 = U_0 + W_1$.

Now we put the system in contact with a heat bath at temperature θ_0 and we change the tension of the applied force back to τ_0. The system, after evolving out of equilibrium, will reach the original equilibrium parametrized by τ_0, θ_0, with length $\mathcal{L}_0$ and energy U_0. The mechanical work done by the force τ_0 is given by $W_0 = \tau_0(\mathcal{L}_0 - \mathcal{L}_1) \neq W_1 = \Delta U$. This means that in this second transformation some energy $Q = W_1 - W_0 = (\tau_1 + \tau_0)(\mathcal{L}_1 - \mathcal{L}_0)$ has been exchanged with the heat bath. We call *heat* this exchanged energy Q. Notice that in principle Q can have both signs.

One can perform different trasformations between these equilibrium states, if they are not adiabatic there will be some heat Q that depends on the particular transformation done. The above transformation was particularly simple and we could compute explicitly Q, also because we knew the energy difference between the two equilibrium states.

This is the content of the first principle of thermodynamics: in first reading it is just energy conservation. We want to maintain the notion of *energy* compatible with the mechanical energy and still a conserved quantity in any transformation. This is also equivalent to say that the energy is a function of the thermodynamic equilibrium state parameter $(\mathcal{L}, \theta)$ (or $(\mathcal{L}, \tau)$) that we call now internal energy [4] and denote it with U.

With the convention adopted here, if we make a transformation that changes from an initial equilibrium $(\mathcal{L}_0, \tau_0)$ to a final $(\mathcal{L}_1, \tau_1)$, the changes of energy is given by

$$U(\mathcal{L}_1, \tau_1) - U(\mathcal{L}_0, \tau_0) = W + Q \tag{1.2.2}$$

Notice that this definition is fine as long as the transformation connects equilibrium states[5].

So $Q > 0$ means heat is flowing into the system, $Q < 0$ it is flowing out of the system.

We insist that *work* and *heat* are determined by specifying the process of

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[4]This in order to distinguish this quantity from the total energy, that could include also the kinetic energy of an eventual mouvement of the center of mass of the system.

[5]In particular Q is the energy (heat) exchanged through the all transormation, while the heat flux at a particular instant of time is not defined.

change, and they are not functions of the state of the system. As we have already said, in mechanics any change of the energy of a system is caused by the *work* done by external forces. If we want to reduce the first principle to a purely mechanical interpretation , this will be the following. The system has many (a very large number) degrees of freedom and many external forces acting on them. Some of these forces, one in our case, are *controlled*, *ordered*, *macroscopic* and *slow*, and the work done by them we still call it **work**: in our case τ is this ordered and controlled slow force, and W the work associated. The other forces are many, *uncontrolled* (or disordered, in the sense that we do not have information on them), *microscopic* and *fast*. The amount of this uncontrolled or disordered work or exchange of energy we call **heat** [6].

One of the main problem of the statistical mechanics interpretation of thermodynamics is to separate the slow macroscopic degree of freedom that generate work from the fast microscopic ones that generate heat. The slow degrees of freedom are generally associated to conserved quantities of the isolated system (with no external forces acting on it or thermal contact with other systems).

In this dynamical interpretation, **the first law** (3.1.17) **defines the separation of microscopic and macroscopic *scales* (in space and time)**. .

1.3   The 1.5 Law: quasi-static transformations

Each thermodynamic law needs concepts and quantities already defined in the previous laws. This is why the 0-law has been introduced: in order to define transitions from an equilibrium to another, we need that different equilibrium states are defined and exist. In order to proceed with the second law, we need now to define and postulate the existence of the quasi-static (or reversible in this context) transformations [7].

Quasi-static, or *reversible*, transformations are defined as trasformations where at each instant the system is at equilibrium for a defined value of the parameters chosen to represent it. So this transformation can be represented as continuous piecewise smooth path on the parameter space (commonly parametrized by $(\tau, \mathcal{L})$, but also (τ, θ) or $(\mathcal{L}, U)$ etc.).

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[6]This will justify the use of *random* forces to model microscopically those forces responsable with their work to produce heat.

[7]Already O.E.Lanford III, in his lectures on 'Mathematical Statistical Mechanics' [6], in the 3rd chapter dedicated to thermodynamics, suggests that the existence of the quasi-static transdformations should be considered an 'axiom' of thermodynamics, even though 'hard to formulate precisely'.

The physical meaning of these quasi-static transformations is a controversial issue. As we have already discussed in the previous section, as we actually change the tension of the cable, the system will go into a sequence of non-equilibrium states before to *relax* to the new equilibrium. But, quoting Zemansky [12], *thermodynamics does not attempt to deal with any problem involving the rate at which the process takes place.* And:

> Every infinitesimal in thermodynamics must satisfy the requirement that it represents a change in a quantity which is small with respect to the quantity itself and large in comparison with the effect produced by the behavior of few molecules.

So we should understand these quasi-static transformations as happening in a *larger* time scale, as limit of a sequence of irreversible infinitesimal non-equilibrium transformations that brings from an equilibrium to a another infinitesimally close one. Later we will construct these quasi-static transformations from a time scaling of concrete non equilibrium trasformations that satisfies a local equilibrium property.

Suppose we have our wire in the thermodynamic equilibrium defined by τ, θ. This can be obtained by applying a tension τ to one extreme and fixing the other to a point, and applying a thermal bath at temperature θ, for example a very large (infinite) system at this temperature on the other side of the *conductive* wall. If we perform infinitesimal changes of these parameters, they imply an infinitesimal variation $d\mathcal{L}$ of the length:

$$d\mathcal{L} = \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_{\tau} d\theta + \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_{\theta} d\tau \tag{1.3.1}$$

These partial derivatives are connected with physical important quantities that can be measured experimentally:

- the *linear dilation coefficient:*

$$\alpha = \frac{1}{\mathcal{L}} \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_{\tau} \tag{1.3.2}$$

  Experimentally it is observed that $\alpha(\tau, \theta)$ depends little by τ, but changes very strongly with θ.

- the *isothermal Young modulus*

$$Y = \frac{\mathcal{L}}{A} \left(\frac{\partial \tau}{\partial \mathcal{L}}\right)_{\theta} \tag{1.3.3}$$

where A is the section of the wire. Experimentally Y depends little on τ and strongly on θ.

We also call $C_\theta = \frac{1}{\mathcal{L}} \left(\frac{\partial \mathcal{L}}{\partial \tau} \right)_\theta$ the isothermal compressibility.

It is an elementary exercise to prove that

$$\left(\frac{\partial \tau}{\partial \mathcal{L}} \right)_\theta \left(\frac{\partial \mathcal{L}}{\partial \theta} \right)_\tau = - \left(\frac{\partial \tau}{\partial \theta} \right)_\mathcal{L} \tag{1.3.4}$$

and consequently

$$\left(\frac{\partial \tau}{\partial \theta} \right)_\mathcal{L} = - \frac{\alpha}{C_\theta} \tag{1.3.5}$$

An infinitesimal variation of the tension can be written in function of $d\theta$ and $d\mathcal{L}$:

$$d\tau = \left(\frac{\partial \tau}{\partial \theta} \right)_\mathcal{L} d\theta + \left(\frac{\partial \tau}{\partial \mathcal{L}} \right)_\theta d\mathcal{L} = -\frac{\alpha}{C_\theta} d\theta + \frac{1}{C_\theta \mathcal{L}} d\mathcal{L} \tag{1.3.6}$$

At constant volume we have

$$d\tau = -\frac{\alpha}{C_\theta} d\theta \tag{1.3.7}$$

Another important exact differential is

$$dU = \left(\frac{\partial U}{\partial \theta} \right)_\tau d\theta + \left(\frac{\partial U}{\partial \tau} \right)_\theta d\tau$$

where $\left(\frac{\partial U}{\partial \theta} \right)_\tau$ is called *heat capacity* (at constant tension).

If the transformation is quasi-static, then we can identify the tension of the system τ as equal as the force applied, obtaining a differential form $\tau d\mathcal{L}$, called differential work. It is clear that this is not an exact differential form, but in thermodynamics books it is used the notation $đW$. This fact is elementary, looking at the path of a transformation in the $(\tau, \mathcal{L})$ coordinates frame. In performing a closed path, that we call *cycle* the path integral $\oint đW \neq 0$ (equal to the area inside the path), and represent the work done on the system by the external force (tension).

During a quasi-static thermodynamic infinitesimal transformation, this energy is modified by the work $đW$ and, since dU has to be an exact differential, by some other (not exact) differential form $đQ$ called *heat exchange*:

$$dU = \tau d\mathcal{L} + đQ \tag{1.3.8}$$

1.3.1 Thermodynamic transformations and cycles

We can compute the canges in a quasi-static thermodynamic transformation by integrating the differential forms defined above along the path. Each choice of a path defines a different *thermodynamic process* or *quasi-static* transformation. Depending on the type of transformation it may be interesting to make a different choice of the coordinates in order to have its graphic representation.

Often is used the $\tau - L$ diagrams.
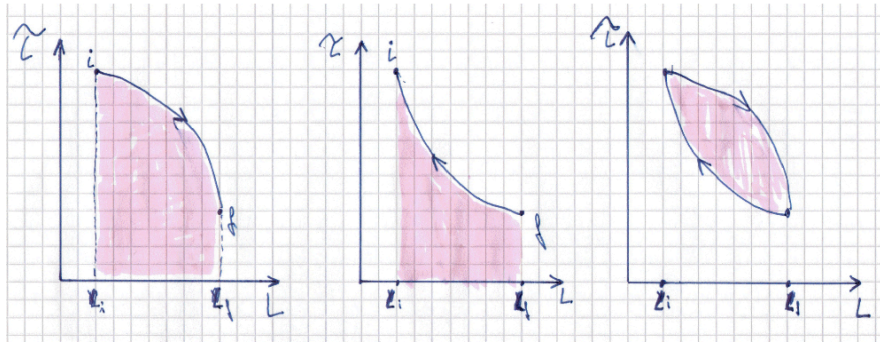
The first diagram on the left describe a quasi-static transformation for length L_i to L_f. The second diagram represent a compression from L_f to L_i, and the third a so called *cycle*, returning to the original state. The shaded area represent the work done during the transformation (taken with the negative sign in the second diagram). In the third the total work done during the entire cycle is given by the integral along the closed path

$$W = \oint \tau dL \tag{1.3.9}$$

that by the first principle will be equal to $-Q$, where Q is the total heat produced by the process during the cycle and transmitted to the exterior (or absorbed by the exterior, depending from the sign). By exterior we mean here another system or an heat bath.

There are some important thermodynamic quasi-static transformation we want to consider:

- *Isothermal transformations*: While a force perform work on the system, this is in contact with a heat bath at the same temperature as the one of the initial equilibrium state of the wire. During a isothermal transformation only the length $\mathcal{L}$ changes as effect of the change of the tension $d\tau$, and the infinitesimal exchanges of heat and work are related by

$$\bar{d}W = \tau d\mathcal{L} = \tau \left(\frac{\partial \mathcal{L}}{\partial \tau} \right)_\theta d\tau = -\bar{d}Q + dU \tag{1.3.10}$$

The isothermal transformations defines isothermal lines parametrized by the temperature. For each value of the temperature correspond an isothermal line of equilibrium states at different tension in the $\tau - \mathcal{L}$ plane, and the 0-law guarantees that these lines do not intersect. Observe that in the quasi-static transformations the tension applied to the system is always equal to the equilibrium tension that the system has in that *instant*. We insists again that the integral defining the work is independent of the time scale of the transformation.

- *Adiabatic transformations*: The system is *thermally isolated* from the exterior. This means that the only force acting on it is given by the tension τ. Equivalently, these are transformations such that $đQ = 0$, and

$$đW = \tau d\mathcal{L} = dU \tag{1.3.11}$$

Adiabatic transformations defines adiabatic lines, but their construction is done by solving the ordinary differential equation

$$\frac{d\tau}{d\mathcal{L}} = \frac{\partial_{\mathcal{L}} U}{\partial_\tau U} \tag{1.3.12}$$

- *Isochore Transformations*: Thermodynamic transformation at fixed length $\mathcal{L}$. Consequently $đW = 0$, no work if performed to or by the system, and

$$đQ = dU \tag{1.3.13}$$

- *Isobar transformations*: Thermodynamic transformation at fixed tension τ, $d\tau = 0$

Special Example: The harmonic (linear) system.

We will encounter a special (ideal) system for which $\tau(L, \theta) = \tau' L$ where τ' is a positive constant. Then $U(L, \theta) = \frac{\tau'}{2} L^2 + \theta$. In this case all isothermal and adiabatic lines in the (L, τ) plane degenerate trivially in a unique straight line $\tau = \tau' L$. In particular adiabatic quasistatic transformation cannot change the temperature.

Carnot Cycles

A Carnot cycle is a cycle composed by a sequence of isothermal and adiabatic quasi–static transformations. In particular is a special machine (or process) that generates (or absorb) work from the heat difference of two heat bath. Different Carnot cycles can be composed in a sequence.

Let us consider the following cycle. The states A,B are at the same temperature θ_2 and C and D at the temperature θ_1. We assume that A and D are in the same adiabatic curve, so are B and C. We perform an θ_2-isothermal transformation from A to B, then an adiabatic from B to C, then a θ_1-isothermal from C to D, then another adiabatic from D to A:
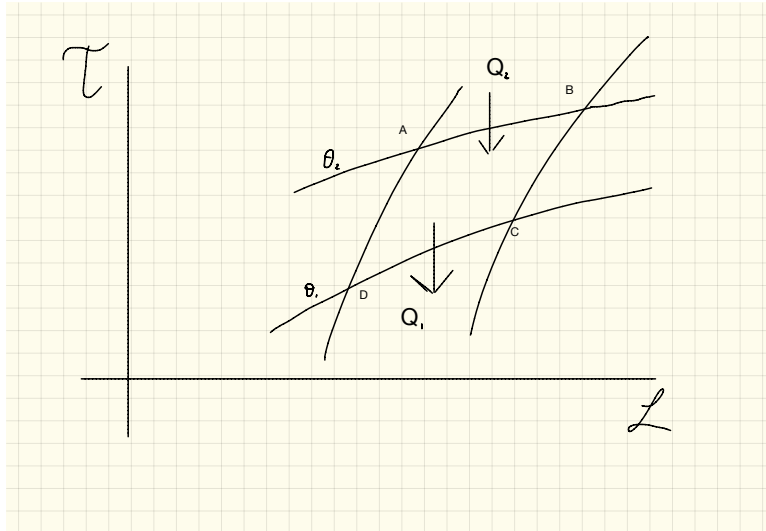
During the isothermal extension of the wire from A to B, it exchange a quantity of heat (energy) Q_2 from the thermostat at temperature θ_2, correspondingly it exchange $-Q_1$ with the thermostat θ_1 during the isothermal transformation CD. Since during adiabatic transformations there is no exchange of heat, during the all cycle the total heat that the system exchange with the exterior is $Q = Q_2 - Q_1$. By the first principle $W + Q = 0$, which means that the heat flown into the system is equal to minus the work done by the tension τ on the system:

$$W = \oint \tau \, d\mathcal{L} = -(Q_2 - Q_1)$$

So, unless $Q_1 = 0$, not all heat Q_2 absorbed from the hot thermostat can be transformed in work.

Notice that for the moment we have not made any assumptions on the signs of Q_1 and Q_2.

Since these are quasi-static trasformations, the cycle is reversible, i.e. we can do all the operations in the reverse order. In this case the the work done is $-W$, the quantity $-Q_1$ is the heat from the thermostat to the system at temperature θ_1 and Q_2 is the one exchanged at temperature θ_2.

If we run the cycle in the opposite direction, i.e. ADCB, the flows are reversed, and the total heat is $-Q = Q_1 - Q_2$ and the work will be equal to Q.

We call *elementary* Carnot cycle the cycle described above. In the following will we compose different *elementary* Carnot cycles in the following way. We can consider two wires, also of different material, so with different state functions, performing the elementary Carnot cycle A'B'C'D'A' or the opposite one A'D'C'B'A' (here these points refer to corresponding points in the isothermal and adiabatic curves of the other system). The composed Carnot cycle will have as total heat produced the sums of the heats and as total work the sum of the works of the elementary cycles.

Also we can consider the same wire operating an elementary Carnot cycle ABCD between the temperature θ_1 and θ_2, with heats Q_1 and Q_2, then operating a Carnot cycle between the states DCEF between temperature θ_0 and θ_1. The composition will give a Carnot cycle between temperatures θ_0 and θ_2, with heats Q_0 and Q_2.

Remark 1.3.1. *Observe that in the linear harmonic material $(\tau(\mathcal{L}, \theta) = \mathcal{L})$, any quasi-static Carnot cycle is trivial: the total work W is always null, as well as $Q_1 = Q_2 = 0$, since it can connect only thermostats at the same temperature (adiabatic quasi-static transformations are unable to change the temperature). We can still consider irreversible Carnot cycles operating between two different temperatures: we can still change* slowly *the tension to perform the quasistatic transformation, but at the moment of connecting the system to the other heat bath, there is a (faster) heat flux equal (or linearly proportional) to the difference of the temperature. The total effect of this irreversible cycle is to transfer equal heat from the hot heat bath to the cold one.*

1.4   The 2nd-Law: Entropy

The second law of thermodynamics has a general statement, due to Lord Kelvin, that is valid for general Carnot cycles, even made with non-quasistatic transformations. The Lord Kelvin statement of the second law is:

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\begin{aligned}
\text{if} \quad W < 0, \quad &\text{then} \quad Q_2 > 0 \quad \text{and} \quad Q_1 > 0 \\
&\text{or} \quad Q_2 < 0 \quad \text{and} \quad Q_1 < 0
\end{aligned}
\tag{1.4.1}
$$

This means that we cannot have $Q_1 \leq 0$ and $Q_2 > 0$ if $W < 0$, i.e. we cannot extract work from the system without giving some heat out during one of the two isothermal transformations. Of course if $W < 0$, the first law already exclude the case $Q_2 < 0$ and $Q_1 > 0$.

Notice that till now, with the empirical definition of temperature given by the 0-Law, we have no way to say what is a higher temperature. Kelvin statement

finally gives us a criteria to say what is the *higher temperature*: we say that $\theta_2 > \theta_1$ if $Q_2 > 0$ and $Q_1 > 0$ when $W < 0$.

Defining the efficiency of the cycle:

$$\eta = \frac{Q}{Q_2} = 1 - \frac{Q_1}{Q_2},$$

an equivalent statement is that $\eta < 1$[8].

More prosaically we say that all Carnot cycles that transforms all heat extracted from the hot reservoir in work (without any heat flow into the cold reservoir) are impossible. Note that, if the cycle is reversible (i.e. quasi static), just reversing the direction of the cycle we have the equivalent statement:

$$\text{if} \quad W > 0, \quad \text{then} \quad Q_2 < 0 \quad \text{and} \quad Q_1 < 0. \tag{1.4.2}$$

The Kelvin statement concern the situations when $W \neq 0$. When $W = 0$, the 1st law says that $Q_2 = Q_1$. The Clausius statement of the second law is [9]:

$$\text{if} \quad W = 0, \quad \text{then} \quad Q_2 = Q_1 \geq 0. \tag{1.4.3}$$

It can be proven that this two statements are equivalent.

Proof that (1.4.3) *implies* (1.4.1):

Consider a cycles, Γ operating between $\theta_2 > \theta_1$. We prove, by contradiction, that if it violate Kelvin statement, then Claudius statement is also violated. Assume that for this cycle $W < 0$ and $Q_1 = 0$, so that $W = -Q_2$, i.e. all heat coming from the hot thermostat is transformed in work. Let us use this work to operate the second Carnot cycle Γ' that operate between the temperature $\theta_1' < \theta_2'$ such that $\theta_1' > \theta_2$. Then the work for Γ' is $W' = -W = Q_2 > 0$. The second cycle will have heat fluxes Q_1', Q_2', and $Q_1' - Q_2' = W' = -W = Q_2 > 0$. But this will imply that the composition of this two cycles will take the heat Q_2 from a thermostat at temperature θ_2 to a thermostat at higher temperature without performing any exterior work, contradicting Clausius statement (1.4.3). $\square$

The Kelvin postulate (1.4.1) has a simple and intuitive statement, but a very deep consequence: it implies the existence of an absolute scale of *temperature*.

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[8]In fact since $0 > W = Q_2 - Q_1$, and Kelvin says that in this situation both Q_1 and Q_2 are strictly positive, then $Q_1 < Q_2$.

[9]Notice that the Clausius statement is trivial for an elementary reversible Carnot cycle. It became an interesting statement only for composite Carnot cycles.

Proposition 1.4.1. *There exists a universal function $f \geq 0$ such that for* **any** *Carnot cycle*

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2) \tag{1.4.4}$$

Proof of proposition 1.4.1.

Consider another Carnot machine operating between the same temperatures θ_1, θ_2, and let be Q'_1, Q'_2 the corresponding heat exchanges. We want to prove that

$$\frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1} \tag{1.4.5}$$

Assume first that the ratio $\frac{Q_2}{Q'_2}$ is a rational number $\frac{N'}{N}$, so that $N'Q'_2 - NQ_2 = 0$. Now we can consider a cycle composed by N' cycles of the second machine and by N cycles *reversed* of the first machine. The total heat exchanged with the thermostat at the (hot) temperature θ_2 by this given by

$$Q_{2,tot} = N'Q'_2 - NQ_2 = 0 \tag{1.4.6}$$

So the total amount of work done in the composed cycle is

$$W_{tot} = Q_{1,tot} = (N'Q'_1 - NQ_1) \tag{1.4.7}$$

By the Kelvin postulate we must have $W_{tot} \geq 0$, that implies

$$N'Q'_1 \geq NQ_1 \tag{1.4.8}$$

that implies

$$\frac{Q_2}{Q_1} \geq \frac{Q'_2}{Q'_1} \tag{1.4.9}$$

To obtain the opposite inequality, we have just to exchange the role of the two machines. The equality (3.4.1) implies that efficiency does not depends on the specific cycle or machine, but only by the temperatures θ_1 and θ_2.

Assume now that $\frac{Q_2}{Q'_2}$ is not rational[10]. By a lemma on the best rational approximation (cf. Sierpinski, Number Theory), there exist two increasing sequences on integers $\{N_k\}_k, \{N'_k\}$ such that

$$0 < \frac{Q_2}{Q'_2} - \frac{N'_k}{N_k} < \frac{1}{N'_k N'_{k-1}} \tag{1.4.10}$$

---

[10]This argument was suggested by Tomasz Komorowski

This implies $0 < N_k Q_2 - N'_k Q'_2 < \frac{Q'_2 N_k}{N'_k N'_{k-1}}$.

We can assume without any restriction, that $W < 0$ and $W' < 0$. In fact if this is not the case, just reverse the corresponding cycle. By Lord Kelvin statement (1.4.1), we have $Q_1, Q'_1, Q_2, Q'_2 > 0$.

Now we let run the second cycle N'_k times and the first cycle N_k times in the reverse direction. The total work is given by $W_k = N'_k W' - N_k W$. Let us assume first that $W_k > 0$ for any k. Then by the first principle we have

$$0 < W_k = -(N'_k Q'_2 - N_k Q_2) + (N'_k Q'_1 - N_k Q_1)$$

By (1.4.10), $N'_k Q'_2 - N_k Q_2 \to 0$ as $k \to \infty$. By the Lord Kelvin statement (1.4.1), $N'_k Q'_1 - N_k Q_1 > 0$, and we obtain

$$N'_k Q'_1 - N_k Q_1 \xrightarrow[k\to\infty]{} 0$$

that implies $\frac{Q_1}{Q'_1} = \frac{Q_2}{Q'_2}$.

Assume now that $W_k \leq 0$. Then

$$\limsup_{k\to\infty} N'_k Q'_1 - N_k Q_1 \leq 0$$

It follows that $\frac{Q_1}{Q'_1} \geq \alpha$. By inverting the role of the machines, i.e. running the first cycle N_k times and then the second cycle N'_k times in the reverse direction we obtain the opposite inequality. $\square$

The above proof does not depends on the order of the temperatures θ_1, θ_2, so we deduce that $f(\theta_1, \theta_2) = f(\theta_2, \theta_1)^{-1}$.

Proposition 1.4.2. *For every θ_0, θ_2, there exists a universal function $g > 0$ such that we have*

$$f(\theta_0, \theta_2) = \frac{g(\theta_2)}{g(\theta_0)} \tag{1.4.11}$$

Proof of (1.6.38) : Consider a third thermostat at temperature θ_1. Let A_1 and A_2 two Carnot cycles working respectively between temperature (θ_1, θ_0) and (θ_2, θ_1). Assume that they are chosen in such a way that the amount of heat Q_1 that they exchange with the thermostat at temperature θ_1 are equal, but Q_1 is in exit for the cycle A_2 and in entrance for the cycle A_2. Then A_1 exchange Q_1 of heat at temperature θ_1, and

$$\frac{Q_1}{Q_0} = f(\theta_0, \theta_1)$$

Similarly for the cycle A_2:

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

and we deduce that

$$\frac{Q_2}{Q_0} = f(\theta_0, \theta_1) f(\theta_1, \theta_2) = \frac{f(\theta_1, \theta_2)}{f(\theta_1, \theta_0)} \tag{1.4.12}$$

But combining the two cycles in sequence, we obtain a cycle that exchange Q_0 with the thermostat at temperature θ_0, and Q_2 to the thermostat at temperature θ_2 (the total heat exchanged with the thermostat θ_1 is null). Consequently for this composite cycle we have

$$\frac{Q_2}{Q_0} = f(\theta_0, \theta_2) \tag{1.4.13}$$

Combining (1.6.38) and (3.3.9),

$$f(\theta_0, \theta_2) = \frac{f(\theta_1, \theta_2)}{f(\theta_1, \theta_0)}$$

and considering that θ_1 is arbitrary in this argument, this quantity does not depend on it and we obtain (1.6.38). $\square$

It follows that there exists a universal function g, defined up to a multiplicative constant, such that

$$\frac{Q_2}{Q_1} = \frac{g(\theta_1)}{g(\theta_2)}$$

This defines an absolute temperature $T = g(\theta)$. The multiplicative constant is the used to define the different scales (Celsius, Farhenait, etc.).

Thermodynamic entropy

Notice that in a simple Carnot cycle we hace $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$ with $T_j = g(\theta_j)$. In terms of the integration of the differential form $\frac{\dbar Q}{T}$, this means

$$\oint \frac{\dbar Q}{T} = 0 \tag{1.4.14}$$

This is also true for a integration on any *composite* Carnot cycle (made by a sequence of isothermal and adiabatic transformations). Since any cycle can be approximated by composite Carnot cycles (exercice), (3.2.2) is actually valid for any cycle, i.e. any closed (peacewise smooth) curve on the state space. Consequently $\frac{\dbar Q}{T}$ is an exact

form, i.e. the differential of a function S of the state of the system. This function is called Thermodynamic Entropy. [11]

If we choose $\mathcal{L}, U$ as parameter determining the state of the system, we have

$$dS = -\frac{\tau}{T} \, d\mathcal{L} + \frac{1}{T} dU \qquad (1.4.15)$$

i.e.

$$\frac{\partial S}{\partial \mathcal{L}} = -\frac{\tau}{T}, \qquad \frac{\partial S}{\partial U} = \frac{1}{T} \qquad (1.4.16)$$

It is also suggestive to use as parameters for the thermodynamic state of the wire S and $\mathcal{L}$, and see the internal energy as function of these because we have

$$dU = \tau d\mathcal{L} + T dS \qquad (1.4.17)$$

so that we can interpret the absolute temperature T as a kind of *thermal* force whose effect is in changing the entropy together with the energy.

1.4.1   2nd law for irreversible transformations

From the consideration in the previous section, adiabatic quasi-static transformations are isoentropic, and only when heat is present entropy can change in quasi-static transformations.

Recall that we have defined *isothermal* non-quasistatic transformations a transformation between two equilibrium states that have the same temperature. This can be tipically realized putting in contact the system with a heat bath of that temperature. For isothermal (non-quasi-static) transformation from an equilibrium state A to another B at the same temperature T, the Kelvin statement implies that

$$Q \leq T \left(S(B) - S(A) \right). \qquad (1.4.18)$$

with equality valid for quasi-static tranformations.

In irreversible (i.e. non-quasistatic) adiabatic transformations ($Q = 0$) we expect an increase of entropy S: $S(B) \geq S(A)$. We will discuss this further in the next section.

---

[11]I never believed the legend about Von Neumann and Shannon: entropy is a well defined physical quantity, like energy, temperature, etc. A quantity that physicist can measure experimentally (at least its variation, like for energy). Physicist knew perfectly what entropy is.

1.5   Intensive and extensive quantities

Imagine our cable in equilibrium be divided in two equal parts (in such a way that the preserve the same boundary conditions that guarantees the original equilibrium). Those quantities that remains the same are called intensive (tension τ, temperature T), while the that are halved are called extensive (trivially the length $\mathcal{L}$, internal energy U, entropy S, ...). We also call the intensive quantities *control parameters*. We will see that when we consider extended systems, dynamically the control parameters and the extensive quantities plays very different role.

1.6   Axiomatic Approach

We can proceed differently and make a more mathematical set-up of the thermodynamics with an axiomatic approach where the extensive quantities $U, \mathcal{L}$ are taken as basic thermodynamic coordinates to identify an equilibrium state and entropy $S(U, \mathcal{L})$ is assumed as a state function satisfying certain properties. This entropy function contains all the information about the (equilibrium) thermodynamic behavior of the system.

It is convenient in this context to add another macroscopic extensive parameter $M > 0$ that represent the *mass* of the system.

axiom-1) There exist an open cone set $\Gamma \subset \mathbb{R}_+ \times \mathbb{R}_+ \times \mathbb{R}$, and $(M, U, \mathcal{L}) \in \Gamma$. This is going to be the set of the equilibrium states of the system.

axiom-2) There exists a C^1–function $S : \Gamma \to \mathbb{R}$ such that

    (i) S is concave,

    (ii) $\frac{\partial S}{\partial U} > 0$,

    (iii) S is positively homogeneous of degree 1:

$$S(\lambda M, \lambda U, \lambda \mathcal{L}) = \lambda S(M, U, \mathcal{L}), \qquad \lambda > 0 \qquad (1.6.1)$$

By 2ii, one can choose eventually S and $\mathcal{L}$ as thermodynamic coordinates, i.e. there exists a function $U(M, S, \mathcal{L})$ such that $\frac{\partial U}{\partial S} > 0$ (exercise).

We call

$$
\begin{aligned}
T &= \frac{\partial U}{\partial S} \qquad \text{temperature} \\
\boldsymbol{\tau} &= \frac{\partial U}{\partial \mathcal{L}} \qquad \text{tension}
\end{aligned}
\qquad (1.6.2)
$$

Exercise: Prove that $U(M, S, \mathcal{L})$ is homogeneous of degree 1 (*extensive*), and $T, \mathcal{L}$ are homogeneous of degree 0 (*intensive*).

Beside this homogeneity property, we can consider M as a constant in the thermodynamic transformations where we are only changing temperatures and/or tension, (unless we are putting different systems together), and we can omit to specify it explicitly. Anyway we adopt here the convention that when M does not appear explicitely in the argument of the thermodinamic functions, it is set $M = 1$ (like $S(U, \mathcal{L}) = S(1, U, \mathcal{L})$).

One can use also the intensive quantities $\boldsymbol{\tau}, T$ as thermodynamic coordinates, and it is useful to define the *Gibbs potential*

$$
\begin{aligned}
\mathcal{G}(T, \boldsymbol{\tau}) &= \sup_{S, \mathcal{L}} \left\{ -T^{-1} U(S, \mathcal{L}) + \frac{\boldsymbol{\tau}}{T} \mathcal{L} + S \right\} \\
&= \sup_{U, \mathcal{L}} \left\{ -T^{-1} U + \frac{\boldsymbol{\tau}}{T} + S(U, \mathcal{L}) \right\}
\end{aligned}
\tag{1.6.3}
$$

Exercice:

$$
S(U, \mathcal{L}) = \inf_{\boldsymbol{\tau}, T} \left\{ \frac{1}{T} U - \frac{\boldsymbol{\tau}}{T} \mathcal{L} + \mathcal{G}(T, \boldsymbol{\tau}) \right\}
\tag{1.6.4}
$$

The differential forms $\bar{d}Q = T dS$ is called *heating*, and $\boldsymbol{\tau} d\mathcal{L}$ *work*. Since $dS = -\frac{\boldsymbol{\tau}}{T} d\mathcal{L} + \frac{1}{T} dU$, it implies that

$$
\bar{d}Q = -\boldsymbol{\tau} d\mathcal{L} + dU
\tag{1.6.5}
$$

Thermodynamic transformations that are quasi-static and reversible, and the corresponding *cycles* are then defined as in the previous sections, and the corresponding work and heat exchange as integrals of these differential forms on the corresponding lines defining the transformations.

Exercice 1.6.1. *Prove that, in a Carnot cycle, Kelvin statement of 2nd principle of thermodynamics follows.*

More controversial is the definition of the *non-reversible* (non-quasi-static) transformations. These are *real* thermodynamic transformations that go from one equilibrium state to another, passing through *non-equilibrium states*.

Usually in thermodynamic books this non-reversible (non-quasi-static) transformations are defined as those where in passing from an initial state $A = (U_0, \mathcal{L}_0)$ to a final state $B = (U_1, \mathcal{L}_1)$ one has the strict inequality

$$
\int_A^B \frac{\bar{d}Q}{T} < S(B) - S(A)
\tag{1.6.6}
$$

This means that in non-equilibrium we cannot identify $đQ/T$ as the exact differential dS. On the other hand the integral on the left hand side of (1.6.6) is not defined mathematically.

For general *isothermal* transformations from an equilibrium state A to another B things are more clearly defined. This imply that A and B are at the same temperature, so we use $(\mathcal{L}, T)$ as parameters of the equilibrium states, and $A = (\mathcal{L}_0, T), B = (\mathcal{L}_1, T)$. The heat Q exchanged with the thermostats is defined by the first law, that means is the difference between the internal energy of the initial and final state and the work done on the system

$$Q = U(B) - U(A) - W.$$

In this case we have

$$Q \leq T\left[S(B) - S(A)\right] \tag{1.6.7}$$

with the equality valid only for *reversible* transformations. This is the irreversible, or non-quasistatic, expression of the second law. It is an upper bound on the amount of heat that can be exchanged during any thermodynamic transformation. Since, by the first principle, the work W exchanged in the transformation is given by $W = [U(B) - U(A)] - Q$, we have

$$-W \leq -[U(B) - U(A)] + T[S(B) - S(A)].$$

this is a limit about the amount of work that can be obtained from such transformation. It is then interesting to define the *free energy* $F(\mathcal{L}, T)$ as

$$F(\mathcal{L}, T) = \inf_{U>0} \left\{U - TS(U, \mathcal{L})\right\} = \inf_{\tau} \left\{\tau\mathcal{L} - T\mathcal{G}(T, \tau)\right\} \tag{1.6.8}$$

This permits to identify $U(\mathcal{L}, T)$ as (*exercice*):

$$U(\mathcal{L}, T) = \partial_T \left(\frac{1}{T}F(\mathcal{L}, T)\right) \tag{1.6.9}$$

or, using $\beta = 1/T$ (that will turn out simpler in statistical mechanics),

$$U(\mathcal{L}, \beta) = \partial_\beta \left(F(\mathcal{L}, \beta^{-1})\right) \tag{1.6.10}$$

that permits to write $\mathcal{F} = U - TS$, without specifying the variables. So for our isothermal transformation:

$$W \geq F(B) - F(A) = \Delta F \tag{1.6.11}$$

In a *reversible* isothermal trasformation we have equality and the work done by the system is equal to the difference of the free energy. In a non reversible one, the difference in free energy is only an upper bound. From (1.6.8) we also obtain

$$\partial_\mathcal{L} F = \tau \ . \tag{1.6.12}$$

In *adiabatic transformations* we have $Q = 0$, and $W = U(B) - U(A)$ like in usual mechanics. Adiabatic reversible (quasi-static) processes are always isoentropic. Still there exists non-reversible adiabatic processes for which $0 = Q < S(B) - S(A)$. Again the identification $đQ = TdS$ has a sense only for reversible quasi-static transformations.

1.6.1 Extended systems and local equilibrium

In order to connect the reversible (quasi-static) statement of the 2nd Law to the irreversible (non-quasistatic) statement (1.6.7), we need some description of the non-equilibriums states where the system goes through these irreversible transformations.

A possible definition of a non-equilibrium state is to consider the system, in our case the wire, as spatially extended, and with different parts of the system in different equilibrium states. For example our wire could be constituted by two different wires, that have the same constitutive materials (i.e. they are make by the same material) and they have *mass* M_1 and M_2 respectively, but they are prepared in two different equilibrium state, parametrized by the extensive quantities: $(U_1, \mathcal{L}_1), (U_2, \mathcal{L}_2)$. The internal energy of the total system composed by the two wires glued together, will be $U_1 + U_2$, while its length will be $\mathcal{L}_1 + \mathcal{L}_2$. Even though the wire is not in equilibrium, we can say that also the other extensive quantities are given by the sum of the corresponding values of each constitutive part in equilibrium, i.e. in the example the entropy will be given by $S(M_1, U_1, \mathcal{L}_1) + S(M_2, U_2, \mathcal{L}_2)$. Notice that concavity and homogeneity properties of S imply

$$
S(M_1, U_1, \mathcal{L}_1) + S(M_2, U_2, \mathcal{L}_2) \leq 2S\left(\frac{M_1 + M_2}{2}, \frac{U_1 + U_2}{2}, \frac{\mathcal{L}_1 + \mathcal{L}_2}{2}\right)
$$
$$
= S(M_1 + M_2, U_1 + U_2, \mathcal{L}_1 + \mathcal{L}_2)
$$

(1.6.13)

This means that the composed wire, of mass $M_1 + M_2$, when in equilibrium with corresponding energy and length values $(U_1 + U_2, \mathcal{L}_1 + \mathcal{L}_2)$, has higher entropy than the sum of the entropy of the two subsystems at different equilibrium values. The equality is valid is $U_1 = U_2$ and $\mathcal{L}_1 = \mathcal{L}_2$.

Consequently if we have a time evolution (dynamics, etc.), that conserves the total energy (*adiabatic transformation*), **and** the total length (*isochore transformation*, the two ends of the wire are fixed), and that brings the total system in a **global** equilibrium, then the final result of this evolution increase the thermodynamic entropy S.

In this framework, the second principle of thermodynamics intended as a strict increase of the thermodynamic entropy if the system undergoes a *non-reversible*

transformation, is related to the property of the isolated system to reach a global equilibrium[12]

More generally we can assign a continuous coordinate $x \in [0, M]$ to each *material* component of the wire (x is **not** the displacement or spacial position of this component). This component (that should be thought as containing a large number of atoms but with total mass $M = 1$) is in equilibrium with an energy $U(x)$ and *stretch* (or *elongation*) $r(x)$. These functions should be thought as *densities*, we call them also *profiles*. The actual spatial displacement (position) of the component x is given by

$$\mathcal{L}(x) = \int_0^x r(x')dx' \tag{1.6.14}$$

The entropy of the component x is given by $S(1, U(x), r(x))$. This class of non-equilibrium states we can call *local equilibrium states* for obvious reasons.

We can associate a total length, energy and entropy to these profiles (i.e. to the corresponding non-equilibrium state):

$$\mathcal{L}_{tot} = \int_0^M r(x)dx, \quad U_{tot} = \int_0^M U(x)dx, \quad S_{tot} = \int_0^M S(1, U(x), r(x))dx. \tag{1.6.15}$$

By concavity of S:

$$S_{tot} \leq MS(1, M^{-1}U_{tot}, M^{-1}\mathcal{L}_{tot}) = S(M, U_{tot}, \mathcal{L}_{tot}) \tag{1.6.16}$$

Usual thermodynamics does not worry about time scales where the thermodynamic processes happens. But in the extended thermodynamics we can consider time evolutions of these profiles (typically evolving following some partial differential equations). The actual time scale in which these evolution occurs with respect to the microscopic dynamics of the atoms, will be the subject of the hydrodynamic limits that we will study in the later chapters.

So if denote by $\dot{r}(x, t)$ and $\dot{U}(x, t)$ the corresponding time derivatives, we have for the time evolution of the entropy:

$$\partial_t S(U(x, t), r(x, t)) = \frac{1}{T}\left(\dot{U} - \boldsymbol{\tau}\dot{r}\right) \tag{1.6.17}$$

We can define the right hand side of (1.6.17) as the instantaneous heat flux. This is well defined only for *regular* (smooth) evolutions.

---

[12]this is related to the dynamical statement of the 0-principle, the property that systems have, in a unidentified time scale, to reach equilibrium once the parameters characterizing the equilibrium states are fixed, here the volume and the energy.

Example: adiabatic evolution, Euler equations

In this evolution, whose deduction from the microscopic dynamics we will study in detail in chapter xx, is given by

$$\partial_t r = \partial_x \pi$$
$$\partial_t \pi = \partial_x \boldsymbol{\tau} \qquad (1.6.18)$$
$$\partial_t U = \partial_x (\boldsymbol{\tau}\pi) - \pi\partial_x\boldsymbol{\tau} = \boldsymbol{\tau}\partial_x\pi$$

These should be implemented by the boundary conditions:

$$\pi(t,0) = 0, \ \boldsymbol{\tau}(U(t,1), r(t,1)) = \bar{\tau}(t) \qquad (1.6.19)$$

where $\bar{\tau}(t)$ is the tension applied at the right boundary at time t.

This means that the material element x, whose position at time t is $\mathcal{L}(x,t)$, has velocity $\pi(x,t) = \partial_t\mathcal{L}(x,t)$. The tension $\boldsymbol{\tau}(U(x,t), \mathcal{L}(x,t))$ is the force acting on the material element x (more precisely the gradient $\partial_x\boldsymbol{\tau}$, since the resulting force is given by the difference of the tension on the right and on the left of the material element). The total energy of the element x is given by $\mathcal{E}(x,t) = U(x,t) + \frac{\pi(x,t)^2}{2}$, the sum of its internal energy and its kinetic energy. The dynamic is adiabatic, so the total energy is changed only by the *work* $\boldsymbol{\tau}\pi$, more precisely by its gradient:

$$\partial_t\mathcal{E} = \partial_x(\boldsymbol{\tau}\pi) \qquad (1.6.20)$$

In particular $\partial_t S(U(x,t), r(x,t)) = 0$, i.e. if the solution is C^1, the entropy is conserved also locally (in the sense that the entropy per component remains unchanged). In fact, in the smooth regime, the equation are time reversible, so they are isoentropic since they are adiabatic.

If one does not consider the effect of the boundary conditions (for example taking periodic b.c.) this system has three conserved quantities ($\int r dx, \int \pi dx, \int \mathcal{E} dx$).

The system (2.3.3) is a non-linear hyperbolic system of equation. It is expected that any nontrivial solution will develop shocks. After appearance of shocks, the equations should be considered in a weak sense and a criterion of choice of the weak solution is that it should have a *positive* production of entropy, where $\partial_t S > 0$ is some weak sense at the position of the shock. A mathematical theorem that guarantee uniqueness of this entropy solution is still lacking. Eventually shocks will create dissipations and the entropy solution, as $t \to \infty$ should converge to a solution with a constant profile of tension $\boldsymbol{\tau}$, i.e. a mechanical equilibrium[13]. Still the system could be in *thermal* non-equilibrium, and consequently (2.3.3) cannot describe the whole adiabatic transformations. Thermal equilibrium will be reached with another

---

[13]actually I could not find any mathematical result is this direction for the Euler system

evolution of the energy, governed by a heat equation or some superdiffusive equation. This means that in an adiabatic trasformations different space-time scales could be involved, with different evolution equations. Since thermodynamics ignore space-time scales, it does not give any prescription about these irreversible evolutions, it is only interested in the initial and final equilibrium state.

Isothermal evolution: diffusion equation

Mathematically things are easier for isothermal transformations.

Consider our wire immersed in a viscous liquid at temperature T uniform, that acts as a heat bath on each element x of the wire. We assume that the action (*thermalization*) due to the heat bath happens in a much faster time scale, so that each material point x of the system is here at temperature T at any time. We also apply a time dependent tension $\tilde\tau(t)$ on the right hand side of the wire, while the left hand side remains attached to a point.

Then we can consider the evolution of the local equilibrium distribution $(U(x,t), r(x,t))$, where the two parameter are depending to each other on the constraint that temperature T is constant in x. Because of the thermalization, velocities of the components of the wire are damped to 0 and it turns out that the evolution is given by the nonlinear diffusion equation:

$$\partial_t r(x,t) = \partial_x^2 \boldsymbol{\tau}(r(x,t),T) \tag{1.6.21}$$

We add the boundary conditions

$$\begin{aligned} \partial_x r(0,t) &= 0 \\ \boldsymbol{\tau}(r(1,t),T) &= \tilde\tau(t) \end{aligned} \tag{1.6.22}$$

We define the free energy of the non-equilibrium profile $\{r(x,t), x \in [0,1]\}$ as

$$\mathcal{F}(t) = \int_0^1 F(r(x,t),T)\, dx \tag{1.6.23}$$

Consider the case where we start our system with a constant tension $\tau(0,x) = \tau_0$ and we apply a tension $\tilde\tau(t)$ going smoothly from $\tilde\tau(0) = \tau_0$ to $\tilde\tau(t) = \tau_1$ for $t \geq t_1$. It follows from standard arguments that

$$\lim_{t\to\infty} \boldsymbol{\tau}(r(t,x),T) = \tau_1, \qquad \forall x \in [0,1] \tag{1.6.24}$$

so on an opportune time scale, this evolution represents an isothermal thermodynamic transformation from the equilibrium state (τ_0, T) to (τ_1, T). Clearly this is an irreversible transformation and will statisfy a strict Clausius inequality.

The length of the system at time t is given by

$$L(t) = \int_0^1 r(t,x) \, dx \qquad (1.6.25)$$

and the work done by the force $\tilde{\tau}$:

$$
\begin{aligned}
W(t) = \int_0^t \tilde{\tau}(s) dL(s) &= \int_0^t ds \, \tilde{\tau}(s) \int_0^1 dx \, \partial_x^2 \boldsymbol{\tau}(r(s,x),T) \\
&= \int_0^t \tilde{\tau}(s) \partial_x \boldsymbol{\tau}(r(s,1),T) ds
\end{aligned}
\qquad (1.6.26)
$$

Thanks to the local equilibrium, we can define the free energy at time t as

$$\mathcal{F}(t) = \int_0^1 F(r(t,x),T) \, dx. \qquad (1.6.27)$$

Its time derivative is (after integration by parts):

$$\frac{d}{dt}\mathcal{F}(t) = -\int_0^1 \left(\partial_x \boldsymbol{\tau}(r(t,x),T)\right)^2 \, dx + \tilde{\tau}(t)\partial_x \boldsymbol{\tau}(r(t,x),T)\big|_{x=1}$$

i.e.

$$\mathcal{F}(t) - \mathcal{F}(0) = W(t) - \int_0^t ds \int_0^1 \left(\partial_x \boldsymbol{\tau}(r(s,x))\right)^2 \, dx$$

Because or initial condition, $\mathcal{F}(0) = F(\tau_0,T)$, and because (1.6.24) we have $\mathcal{F}(t) \to F(\tau_1,T)$, and we conclude that

$$F(\tau_1,T) - F(\tau_0,T) = W - \int_0^{+\infty} ds \int_0^1 \left(\partial_x \boldsymbol{\tau}(r(s,x),T)\right)^2 \, dx \qquad (1.6.28)$$

where W is the total work done by the force $\tilde{\tau}$ in the transformation up to reaching the new equilibrium and is expressed by taking the limit in (1.6.26) for $t \to \infty$:

$$W = \int_0^\infty \tilde{\tau}(s) dL(s) = \int_0^\infty \tilde{\tau}(s)\partial_x \boldsymbol{\tau}(r(s,1),T) ds \qquad (1.6.29)$$

By the same argument we will use in the proof of Proposition 1.6.2 we have that the second term of the righthand side of (1.6.28) is finite, that implies the existence of W.

Since the second term on right hand side is always strictly positive, we have obtained a strict Clausius inequality. This is not surprising since we are operating an irreversible transformation.

If we want to obtain a *reversible quasistatic isothermal transformation*, we have introduce another larger time scale, i.e. introduce a small parameter $\varepsilon > 0$ and apply a tension slowly varying in time $\tilde{\tau}(\varepsilon t)$. The diffusive equation becomes

$$\partial_t r_\varepsilon(t, x) = \partial_x^2 \boldsymbol{\tau}(r_\varepsilon(t, x), T) \tag{1.6.30}$$

with boundary conditions

$$\begin{aligned} \partial_x r_\varepsilon(t, 0) &= 0 \\ \boldsymbol{\tau}(r_\varepsilon(t, 1), T) &= \tilde{\tau}(\varepsilon t) \end{aligned} \tag{1.6.31}$$

Then (1.6.28) became

$$F(r_1, T) - F(r_0, T) = W_\varepsilon - \int_0^\infty ds \int_0^1 (\partial_x \boldsymbol{\tau}(r_\varepsilon(s, x), T))^2 \ dx \tag{1.6.32}$$

In order to simplify the proof of the quasistatic limit, let us assume that

$$0 < C_1 \leq \tilde{\tau}'(r) \leq C_2 < \infty \tag{1.6.33}$$

which is a natural assumption on the strict diffusivity of the equation (1.6.21).

Since T is constant, we will drop the dependences on it in the following.

Proposition 1.6.2. *Assume* (2.3.1). *Then*

$$\lim_{\varepsilon \to 0} \int_0^\infty ds \int_0^1 (\partial_x \boldsymbol{\tau}(r_\varepsilon(s, x)))^2 \ dx = 0 \tag{1.6.34}$$

Proof. We look at the time scale $\mathfrak{t} = \varepsilon^{-1} t$, then $\tilde{r}_\varepsilon(\mathfrak{t}, x) = r_\varepsilon(\varepsilon^{-1}t, x)$ statisfy the equation

$$\partial_{\mathfrak{t}} \tilde{r}_\varepsilon(\mathfrak{t}, x) = \varepsilon^{-1} \partial_x^2 \boldsymbol{\tau}(\tilde{r}_\varepsilon(\mathfrak{t}, x)) \tag{1.6.35}$$

with boundary conditions

$$\begin{aligned} \partial_x r_\varepsilon(\mathfrak{t}, 0) &= 0 \\ \boldsymbol{\tau}(r_\varepsilon(\mathfrak{t}, 1)) &= \tilde{\tau}(\mathfrak{t}) \end{aligned} \tag{1.6.36}$$

$$\begin{aligned} \frac{1}{2} \int_0^1 & (\tilde{r}_\varepsilon(\mathfrak{t}, x) - \mathfrak{r}[\tilde{\tau}(\mathfrak{t})])^2 \, dx \\ &= \int_0^{\mathfrak{t}} ds \int_0^1 dx \ (\tilde{r}_\varepsilon(s, x) - \mathfrak{r}(\tilde{\tau}(s))) \left(\varepsilon^{-1} \partial_x^2 \boldsymbol{\tau}[\tilde{r}_\varepsilon(s, x)] - \frac{d}{ds}\mathfrak{r}[\tilde{\tau}(s)] \right) \\ &= -\varepsilon^{-1} \int_0^{\mathfrak{t}} ds \int_0^1 dx \ (\partial_x \tilde{r}_\varepsilon(s, x))^2 \frac{d\boldsymbol{\tau}}{dr}[\tilde{r}_\varepsilon(s, x)] \\ &\quad - \int_0^{\mathfrak{t}} ds \frac{d\mathfrak{r}}{d\tau}(\tilde{\tau}(s)) \tilde{\tau}'(s) \int_0^1 dx \ (\tilde{r}_\varepsilon(s, x) - \tilde{r}_\varepsilon(s, 1)) \end{aligned} \tag{1.6.37}$$

Rewriting

$$\left| \int_0^1 dx \ (\tilde{r}_\varepsilon(s,x) - \tilde{r}_\varepsilon(s,1)) \right| = \left| \int_0^1 dx \ \int_x^1 dy \ \partial_y \tilde{r}_\varepsilon(s,y) \right|$$

$$= \left| \int_0^1 dy \ y \partial_y \tilde{r}_\varepsilon(s,y) \right| \leq \frac{\alpha}{2\varepsilon} \int_0^1 dx \ (\partial_x \tilde{r}_\varepsilon(s,x))^2 + \frac{\varepsilon}{6\alpha}$$

By our assumption we have $0 < C_- \leq \frac{d\mathfrak{t}}{d\tau} \leq C_+ < +\infty$, and furthermore we have chosen $\tilde{\tau}$ such that $|\tilde{\tau}'(t)| \leq 1_{t \leq t_1}$. Regrouping positive terms on the left hand side we obtain the bound:

$$\frac{1}{2} \int_0^1 (\tilde{r}_\varepsilon(\mathfrak{t},x) - \mathfrak{r}[\tilde{\tau}(\mathfrak{t})])^2 \, dx + \varepsilon^{-1}\left(C_- - \frac{\alpha}{2C_-}\right) \int_0^{\mathfrak{t}} ds \int_0^1 dx \ (\partial_x \tilde{r}_\varepsilon(s,x))^2 \leq \frac{\varepsilon t_1}{6\alpha C_-} \tag{1.6.38}$$

By choosing $\alpha = C_-^2$, we obtain, for any $\mathfrak{t} > t_1$:

$$\frac{1}{C_-} \int_0^1 (\tilde{r}_\varepsilon(\mathfrak{t},x) - \mathfrak{r}[\tilde{\tau}(t_1)])^2 \, dx + \varepsilon^{-1} \int_0^{\mathfrak{t}} ds \int_0^1 dx \ (\partial_x \tilde{r}_\varepsilon(s,x))^2 \leq \varepsilon \frac{t_1}{3C_-^4} \tag{1.6.39}$$

then we can take the limit as $\mathfrak{t} \to \infty$, the first term on the right hand side of (3.3.9) will disappear, and we obtain

$$\varepsilon^{-1} \int_0^{+\infty} ds \int_0^1 dx \ (\partial_x \tilde{r}_\varepsilon(s,x))^2 \leq \varepsilon \frac{t_1}{3C_-^4} \tag{1.6.40}$$

that implies (1.6.34). $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\square$

Consequently we obtain the Clausius identity for the quasistatic reversible isothermal transformation.

Along the lines of the proof above it is also easy to prove that

$$\lim_{\varepsilon \to 0} \int_0^1 (r_\varepsilon(t,x) - \mathfrak{r}[\tilde{\tau}(\varepsilon t)])^2 \, dx = 0 \tag{1.6.41}$$

that gives a rigorous meaning to the *quasistatic* definition.

Recall that internal energy of the thermodynamic equilibrium state (r,T) is given by $U = F + TS$, where S is the thermodynamic entropy, and that the first principle of thermodynamics defines the heat Q transferred as $\Delta U = W + Q$.

The change of internal energy in the isothermal transformation is given by

$$\Delta U = \Delta F + T\Delta S = W - \int_0^{+\infty} ds \int_0^1 dx \ (\partial_x \boldsymbol{\tau}(r(s,x),T))^2 + T\Delta S \tag{1.6.42}$$

Then for the irreversible transformation we have $Q \leq T\Delta S$, while equality holds in the quasistatic limit.

The linear case is special, it corresponds to the microscopic harmonic interaction. In this case S is just a function of the temperature ($S \sim \log T$), so $\Delta S = 0$ for any isothermal transformation. Correspondingly the heat exchanged with the thermostat is always negative and given by $Q = -\int_0^{+\infty} ds \int_0^1 dx \; (\partial_x r(s, x))^2$, and null in the quasistatic limit, in agreement with remark Theorem 1.3.1.

1.7   Some comments on the literature

The number of books on thermodynamics, at every level, are almost uncountable. I mention here only some that I encountered, in our education and recently in preparing this text. Even though it is fascinating to compare the different point of view, a complete picture is impossible, and beyond our interest.

Probably the most popular book on thermodynamics between the physicist is the one of Fermi [4], reprint of the notes of the course he gave at Columbia University in 1936.

The textbook of Zemansky [12] is a classic where generations of students learnt thermodynamics at the first year, including myself. Particularly impressive is the description of all type of thermometers at the beginning of the book.

Callen's book [1] is more *theoretical* and assiomatic.

The treatise of Planck [10] has historical interest. At the end of the introduction to the first edition (1897), there is a funny comment: *Although it may be of advantage for a time to consider the activities of nature –Heat, Motion, Electricity, etc– as different in quality, and suppress the question as to their common nature, still our aspiration after a uniform theory of nature, on a mechanical basis or otherwise ... can never be permanently repressed.* And Planck continues predicting that in the *future* the two laws of thermodynamics will be deduced from other *more general propositions*. Only in the introduction to the second edition (1905), Planck will mention the word *probability*.

Many authors tried a rigorous mathematical approach (or at least satisfactory for a mathematician). The lecture notes by Evans [3] are quite interesting, and contains many references at different approach. These notes, quite original, are unpublished (probably Evans felt unsatisfied by the state of the matter) and can be found on his web page. Particularly interesting is the connection with the EDP, viscous solutions, large deviation, etc.

Chapter 2

One dimensional chain of oscillators: equilibrium distributions

2.1 Canonical dynamics (isobar)

We study a system of $m = [nM]$ anharmonic oscillators, where $M > 0$ is a positive parameter corresponding to the macroscopic mass of the total system. The particles are denoted by $j = 1, \ldots m$. We denote with $q_j, j = 1, \ldots, m$ their positions, and with p_j the corresponding momentum (which is equal to its velocity since we assume that all particles have mass 1). We consider first the system attached to a *point* on the left side, and we set $q_0 = 0, p_0 = 0$. Between each pair of consecutive particles $(i, i+1)$ there is an anharmonic spring described by its potential energy $V(q_{i+1} - q_i)$. We assume V is a positive smooth function such that $V(r) \to +\infty$ as $|r| \to \infty$ and such that

$$\int e^{-\beta(V(r) - \tau r)} dr < +\infty \tag{2.1.1}$$

for all $\beta > 0$ and all $\tau \in \mathbb{R}$. It is convenient to work with interparticle distance as coordinates, rather than absolute particle position, so we define

$$r_j = q_j - q_{j-1}, \qquad j = 1, \ldots, m.$$

The position of the particle m, which is also the total length of the chain, is given by $q_m = \sum_{j=1}^{m} r_j$.

The configuration of the system is given by $\{p_j, r_j, j = 1, \ldots, m\} \in \mathbb{R}^{2m}$, and

energy function (Hamiltonian) defined on each configuration is given by

$$\mathcal{H} = \sum_{j=1}^{m} \mathcal{E}_j$$

where

$$\mathcal{E}_j = \frac{1}{2}p_j^2 + V(r_j), \quad j = 1, \ldots, m$$

is the energy of each oscillator. This choice is a bit arbitrary, because we associate the potential energy of the bond $V(r_j)$ to the particle j. Different choices can be made, but this one is notationally convenient.

We will study here the equilibrium distribution of this chain under different boundary conditions.

In the isobaric dynamics, we apply on the particle m a constant force $\tau \in \mathbb{R}$ (tension). The Hamiltonian dynamics is the given by:

$$\begin{aligned}
\dot{r}_j(t) &= p_j(t) - p_{j-1}(t), & j &= 1, \ldots, m, \\
\dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), & j &= 1, \ldots, m-1, & (2.1.2) \\
\dot{p}_m(t) &= \tau - V'(r_m(t)),
\end{aligned}$$

Define

$$G(\tau, \beta) = \log\left[\sqrt{2\pi\beta^{-1}} \int e^{-\beta(V(r) - \tau r)} dr\right]. \tag{2.1.3}$$

It is easy to see that, for any $\beta > 0$, the canonical measure $\mu_{\tau,\beta}^{c,m}$ defined by

$$d\mu_{\tau,\beta}^{c,m} = \prod_{j=1}^{m} e^{-\beta(\mathcal{E}_j - \tau r_j) - \mathcal{G}(\tau,\beta)} dr_j dp_j \tag{2.1.4}$$

is stationary for this dynamics.

The distribution $\mu_{\tau,\beta}^{c,m}$ is called canonical Gibbs measure at temperature $T = \beta^{-1}$ and tension (or pressure) τ (we will refer to this also as the isobaric canonical Gibbs measure). Notice that $\{r_1, \ldots, r_m, p_1, \ldots, p_m\}$ are independently distributed under this probability measure.

We have the following immediate relations:

$$\beta^{-1} = \int p_j^2 \, d\mu_{\tau,\beta}^{c,m}, \qquad \tau = \int V'(r_j) \, d\mu_{\tau,\beta}^{m,c} \tag{2.1.5}$$

and the average elongation and energy in the canonical measure:

$$\begin{aligned}
\mathcal{L}(\tau, \beta) &= \beta^{-1}\frac{\partial \mathcal{G}(\tau, \beta)}{\partial \tau} = \int r_j \, d\mu_{\tau,\beta}^{c,m} \\
U(\lambda, \beta) &= -\frac{\partial \mathcal{G}(\tau, \beta)}{\partial \beta} = \int V(r_j) d\mu_{\tau,\beta}^{c,m} + \frac{1}{2\beta} = \int \mathcal{E}_j \, d\mu_{\tau,\beta}^{c,m}
\end{aligned} \tag{2.1.6}$$

2.1.1 Stochastic thermostats

One way to select one value of the inverse temperature is to put the chain in contact with a heat bath at temperature β^{-1}. A very efficient microscopic model for a heat bath is given by the Langevin stochastic dynamics:

$$\dot{r}_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1, \ldots, m,$$
$$dp_j(t) = (V'(r_{j+1}(t)) - V'(r_j(t)))\, dt - \gamma_j p_j\, dt + \sqrt{2\gamma_j \beta^{-1}}\, dw_j(t), \qquad j = 1, \ldots, m-1,$$
$$dp_m(t) = (\tau - V'(r_m(t)))\, dt - \gamma_m p_m\, dt + \sqrt{2\gamma_m \beta^{-1}}\, dw_m(t),$$

$$(2.1.7)$$

where $\gamma_j \geq 0$ are coupling parameters with the thermostats, and $w_m(t)$ are independent standard Wiener processes, with dw_j indicating the Ito's stochastic differential.

It is enough that $\gamma_j > 0$ for at least one j (for example at $j = m$), to have a unique stationary measure given by $\mu_{\tau,\beta}^{c,m}$. So we can consider heath bath acting only at boundaries or in the bulk: the equilibrium measure will be the same, but the time scales to reach equilibrium will be different. We will see this aspect more carefully later.

Another model for ideal thermostat, that actually derive from a deterministic dynamics, but infinite, is the following. Imagine that each particle j of our system is in contact with a heat bath constituted by infinitely many non-interacting particles that have velocity distributed independently by a centered gaussian distribution with variance β^{-1} and position randmply distributed by a Poisson distribution with density depending of $\gamma_j \geq 0$ (if $\gamma_j = 0$ the heat bath is empty and does not act on the system). When the particles of the heat bath collide with the particle j of our chain, they exchange velocity, as in an elastic collision. Without following the trajectory of the particles of the heat bath, this evolution is completely equivalent to the following (jump) stochastic differential equations:

$$\dot{r}_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1, \ldots, m,$$
$$dp_j(t) = (V'(r_{j+1}(t)) - V'(r_j(t)))\, dt - (p_j(t^-) - \tilde{p}_{j,N_j(t)})dN_j(t) \qquad i = 1, \ldots, m-1,$$
$$dp_m(t) = (\bar{\tau}(t) - V'(r_m))\, dt - (p_m(t^-) - \tilde{p}_{m,N_m(t)})dN_m(t),$$

$$(2.1.8)$$

where $N_j(t)$ are independent Poisson processes with intensity γ_j (that give the random times of the renewals of the velocities), and $\{\tilde{p}_{j,h}, j = 1, \ldots, m; h \in \mathbb{N}\}$ are i.i.d. random variables $\mathcal{N}(0, \beta^{-1})$ distributed.

The jump heat bath model used in equations (2.1.8) are a bit *slower* in driving the dynamics towards thermal equilibrium than the Langevin one used in (2.1.7). On the other hand (2.1.7) can be obtained in some scaling limit from (2.1.8).

2.2 Microcanonical Dynamics

Instead of applying a force (tension) to one side of the chain, one can fix the last particle m to another wall at distance $m\mathcal{L}$ ($q_n = \sum_{j=1}^{m} r_j = m\mathcal{L}$ and $p_m = \dot{p}_m = 0$). The dynamics now is conserving the total energy $\mathcal{H} = \sum_j \mathcal{E}_j = mU$ and the total length $\sum_{j=1}^{m} r_j = m\mathcal{L}$:

$$
\begin{aligned}
\dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \ldots, m-1, \\
\dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j = 1, \ldots, m-1, \\
r_n(t) &= m\mathcal{L} - \sum_{j=1}^{m-1} r_j(t) \, .
\end{aligned}
\tag{2.2.1}
$$

Recall we have set $m = [nM]$. For $M > 0, U > 0, \mathcal{L} \in \mathbb{R}$, we have the microcanonical surface

$$
\tilde{\Sigma}_n(M, MU, M\mathcal{L}) := \left\{ (r_1, p_1, \ldots, r_m, p_m) : \frac{1}{n} \sum_{j=1}^{m} \mathcal{E}_j = MU, \frac{1}{n} \sum_{j=1}^{m} r_j = M\mathcal{L} \right\}
$$
$$
\sim \Sigma_m(U, \mathcal{L}) = \left\{ (r_1, p_1, \ldots, r_m, p_m) : \mathcal{E}^{(m)} = U, r^{(m)} = \mathcal{L} \right\}.
\tag{2.2.2}
$$

where $\mathcal{E}^{(m)} := \frac{1}{m} \sum_{j=1}^{m} \mathcal{E}_j$ and $r^{(m)} := \frac{1}{m} \sum_{j=1}^{m} r_j$, and the $\sim$ indicates that the difference is negligeable for $n \to \infty$.

Defining $W_m(U, \mathcal{L})$ the total volume of $\Sigma_m(U, \mathcal{L})$ measured by the projection of the Lebesque measure on $\mathbb{R}^{2m}$. This is defined by the following formula

$$
\int F(\mathcal{E}^{(m)}, r^{(m)}) \prod_{i=1}^{m} dr_j dp_j = \int_{\mathbb{R}} dr \int_{\mathbb{R}_+} du \, F(r, u) \, W_m(u, r),
\tag{2.2.3}
$$

for any integrable bounded $F(u, r)$ defined on $\mathbb{R}_+ \times \mathbb{R}$. We call $W_m(U, \mathcal{L})$ the microcanonical volume of the configurations with total energy mU and total length $m\mathcal{L}$. By an easy subadditive argument the following limit exists

$$
S(M, MU, M\mathcal{L}) := \lim_{n \to \infty} \frac{1}{n} \log W_m(U, \mathcal{L}) = MS(1, U, \mathcal{L})
\tag{2.2.4}
$$

In fact by the definition follows that S is homogeneous of degree 1. Since often we work with total mass $M = 1$, in the following we use the notation $S(U, \mathcal{L}) = S(1, U, \mathcal{L})$. We want to indentify this function as the *thermodynamic entropy*. It can be proven that (see appendix A) that

$$
S(U, \mathcal{L}) = \inf_{\tau, \beta > 0} \left\{ -\beta \tau \mathcal{L} + \beta U - \mathcal{G}(\beta^{-1}, \tau) \right\}.
\tag{2.2.5}
$$

These are the fundamental relations that connects the microscopic system to its thermodynamic macroscopic description[1].

The limit in (2.2.4) is intended for all values of the internal energy $U > 0$. Clearly from the definition of $\Sigma_m(U, \mathcal{L})$, it follows that $S(U, \mathcal{L}) \to -\infty$ if $U \to 0$[2].

S is concave, since inf of linear functions.

We can now define the other thermodynamic quantities from the entropy definition (2.2.5). From equation (2.2.5) we obtain the inverse of (2.1.6):

$$\beta(\mathcal{L}, U) = \frac{\partial S(\mathcal{L}, U)}{\partial U} \qquad \tau(\mathcal{L}, U) = -\beta(\mathcal{L}, U)^{-1}\frac{\partial S(\mathcal{L}, U)}{\partial \mathcal{L}}, \qquad (2.2.6)$$

Computing the total differential of $S(r, u)$ we have

$$dS(U, \mathcal{L}) = -\beta\tau d\mathcal{L} + \beta dU = \frac{\text{d}Q}{T} \qquad (2.2.7)$$

where $\text{d}Q$ is the (non-exact) differential [3]

$$\text{d}Q = -\tau d\mathcal{L} + dU. \qquad (2.2.8)$$

Example: In the chain of harmonic oscillators, $\Sigma_m(U, \mathcal{L})$ is a $2m-2$-dimensional sphere whose surface can be computed explicitely and

$$S(U, \mathcal{L}) = 1 + \log \pi + \log \left(U - \frac{\mathcal{L}^2}{2} \right) = 1 + \log \pi + \log \beta^{-1}(U, \mathcal{L}) \qquad (2.2.9)$$

and we have

$$\beta = \frac{\partial S}{\partial U}, \qquad \beta\tau = -\frac{\partial S}{\partial \mathcal{L}} = \mathcal{L}. \qquad (2.2.10)$$

We can now define the microcanonical measures $\mu_{\mathcal{L}, U}^{mc, n}$. Consider the vector valued i.i.d. random variables

$$\{\mathbf{X}_j = (r_j, \mathcal{E}_j), j = 1, \ldots, n\},$$

---

[1]We can recognize (2.2.4) as the celebrated Boltzmann formula $S = k \log W$. Even though no limit was taken in Boltzmann formula, recall that $k = \frac{R}{N_A} = 1.3810^{-23} J/K$

[2]This would be in contradiction with the 3rd-Law, in the Planck formulation, that requires microscopically a quantum dynamics deduction.

[3](2.2.8) and (2.2.7) are analogous to the corresponding differential expressions of the 1st and 2nd law we encountered in the previous chapter in thermodynamics. But for the moment this is only a *thermodynamic analogy*, as Gibbs called it [5]. We still need some dynamical argument to indentify S with the Clausius entropy we have defined using Carnot cycles.

distributed by $d\mu^{c,n}_{\tau_0,\beta_0}$. Fix $\mathbf{x} = (\mathcal{L}, U)$, and define $\mu^{mc,n}_{\mathbf{x}}$ the conditional distribution of $(r_1, p_1, \ldots, r_n, p_n)$ on the manifold $\sum_{j=1}^{n} \mathbf{X}_j = n\mathbf{x}$. This is defined, for any bounded continuous function $G : \mathbb{R} \times \mathbb{R}_+ \to \mathbb{R}$ and $H : \mathbb{R}^{2n} \to \mathbb{R}$, by

$$\int G(\hat{\mathbf{S}}_n) H(r_1, p_1, \ldots, r_n, p_n) \, d\mu^{c,n}_{\tau_0,\beta_0}(r_1, p_1, \ldots, r_n, p_n)$$

$$= \int_{\mathbb{R}\times\mathbb{R}_+} d\mathbf{x}\, G(\mathbf{x}) f_n(\mathbf{x}) \int H(r_1, p_1, \ldots, r_n, p_n) \, d\mu^{mc,n}_{\mathbf{x}}(r_1, p_1, \ldots, r_n, p_n | \mathbf{x})$$

where $\hat{\mathbf{S}}_n = \frac{1}{n} \sum_{i=1}^{n} \mathbf{X}_i$. It is easy to see that $\mu^{mc,n}_{\mathbf{x}}$ does not depend on τ_0, β_0. We call $\mu^{mc,n}_{\mathbf{x}}$ the *microcanonical measure*.

It is not hard to prove that microcanonical measures are stationary for the microcanonical dynamics defined by (2.2.1). This is in fact a consequence that Lebesgue measure is stationary for the hamiltonian dynamics (2.2.1), so is any projection of this measure on a surface defined by a constant value of conserved quantities.

One of the main difficulties is that, in particular for smooth interaction V, there could be other conserved quantities than the elongation $r^{(n)}$ and the energy $\mathcal{E}^{(n)}$, and correspondingly other invariant measures. For finite n this is typical, but we expect that as $n \to \infty$, *relevant* conserved quantities would *disappear*, in some sense, except for energy and elongation. This requires some precision, as in the corresponding infinite dynamics, the concept of conserved quantity is not well defined. This *ergodicity* property of the infinite dynamics will be characterised by the uniqueness of the stationary measures: for the infinite dynamics we would like that all stationary measure are given by convex combination of limits of microcanonical measures, that in this limit these will be equivalent to canonical measure (see below statement). We will study this property more carefully in a next chapter. We have no determionistic Hamiltonian dynamics where this property can be proven, on the contray we have some couterexample constituted by completely integrable dynamics. In the harmonic case $V(r) = r^2/2$, the dynamics is completely integrable and there are $2n$ integral of the motion. Another case is the Toda lattice interaction $V(r) = e^{-\alpha r} - r$. *We will discuss extensively later this point.*

Equivalence between microcanonical and canonical measures:

Theorem 2.2.1. *Given* $\mathbf{x} = (\mathcal{L}, U)$, *let*

$$\beta = \beta(\mathcal{L}, U) = \frac{\partial S}{\partial U}, \qquad \tau = \tau(\mathcal{L}, U) = -\beta^{-1}\frac{\partial S}{\partial \mathcal{L}}.$$

Then for any bounded continuous function $F : \mathbb{R}^{2k} \to \mathbb{R}$ we have

$$\lim_{n \to \infty} \int F(r_1, p_1, \ldots, r_k, p_k) \, d\mu_{\mathbf{x}}^{mc,n}(r_1, p_1, \ldots, r_n, p_n)$$

$$= \int F(r_1, p_1, \ldots, r_k, p_k) \, d\mu_{\tau,\beta}^{c,k}(r_1, p_1, \ldots, r_k, p_k)$$

It will be useful later the equivalence of ensembles in the following stronger form:

Theorem 2.2.2. *Under the same conditions of Theorem 2.2.1, assume that*

$$\int F(r_1, p_1, \ldots, r_k, p_k) \, d\mu_{\tau,\beta}^{k,c}(r_1, p_1, \ldots, r_k, p_k) = 0.$$

Then

$$\lim_{n \to \infty} \int \left| \frac{1}{n-k} \sum_{i=1}^{n-k} F(r_i, p_i, \ldots, r_{i+k}, p_{k+i}) \right| d\mu_{\mathbf{x}}^{n,mc} = 0$$

The proof of these two theorems can be found in Appendix xx.

2.3 Local equilibrium, local Gibbs measures

The Gibbs distributions defined in the above sections are the equilibrium distributions for the dynamics. Studying the non-equilibrium behaviour we need the concept of *local equilibrium* distributions. These are probability distributions that have some asymptotic properties when the system became large ($n \to \infty$), vaguely speaking *locally* they look like Gibbs measure. We need a more precise mathematical definition, that will be useful later for proving macroscopic behaviour of the system.

Definition 2.3.1. *Given two functions, an inverse-temperature profile $\beta(y) > 0$ and a tension profile $\tau(y), y \in [0, 1]$, we say that the sequence of probability measures μ_n on $\mathbb{R}^{2n}$ has the local equilibrium property (with respect to the profiles $\beta(\cdot), \tau(\cdot)$) if for any $k > 0$ and $y \in (0, 1)$,*

$$\lim_{n \to \infty} \mu_n \big|_{([ny],[ny]+k)} = \mu_{\tau(y),\beta(y)}^{c,k} \tag{2.3.1}$$

where $\mu_n \big|_{([ny],[ny]+k)}$ denote the marginal of μ_n on $\{r_{[ny]}, p_{[ny]}, \ldots, r_{[ny]+k-1}, p_{[ny]+k-1}\}$.

Sometimes we will need some weaker definition of local equilibrium (for example relaxing the pointwise convergence in y). It is important here to understand that *local equilibrium* is a property of a *sequence* of probability measures.

The most simple example of local equilibrium sequence is given by the local Gibbs measures:

$$\prod_{j=1}^{n} e^{-\beta(j/n)(\mathcal{E}_j - \tau(j/n)r_j) - \mathcal{G}(\beta(j/n)^{-1}, \tau(j/n))} \, dr_j dp_j = g^n_{\tau(\cdot), \beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j \qquad (2.3.2)$$

Of course are local equilibrium sequences also *small order* perturbations of this sequence like

$$e^{\frac{1}{n} \sum_j F_j(r_{j-h}, p_{j-h}, \ldots, r_{j+h}, p_{j+h})} g^n_{\tau(\cdot), \beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j \qquad (2.3.3)$$

where F_j are local bounded functions.

To a local equilibrium sequence we can associate a thermodynamic entropy, defined as

$$S(r(\cdot), u(\cdot)) = \int_0^1 S(r(y), u(y)) \, dy \qquad (2.3.4)$$

where $r(y), u(y)$ are computed from $\tau(y), \beta(y)$ using (2.1.6). We then can use all the definitions and results of section 21.

Chapter 3

Isothermal transformations

In this chapter we obtain a thermodynamic isothermal transformations from the space-time rescaling of the microscopic dynamics of the chain in contact with a heat bath at temperature β^{-1}, as defined in section 2.1.1. We consider the situation where the heat bath acts uniforly in the all bulk of the chain, and the tension applied to the last particle is time dependent (varying slowly, in the macroscopic scale). While the variance of the velocities will tend to be close to the temperature of the heat bath in a very short time scale, the elongation or stretch of the chain, that is a conserved quantity in the bulk of the chain, will evolve slowly and we need to look at a diffusive space-time scale to see a relaxation to equilibrium that is governed by a diffusive equation, eventually non-linear if thermodynamic tension is a non-linear function of the length. Changing the scale dependence of the tension to a slower one, we obtain the quasistatic isothermal transformations.

3.1 Isothermal microscopic dynamics

We assume V to be a positive smooth function which for large r grows faster than linear but at most quadratic, that means that there exists a constant $C > 0$ such that

$$\lim_{|r|\to\infty} \frac{V(r)}{|r|} = \infty. \tag{3.1.1}$$

$$\limsup_{|r|\to\infty} V''(r) \leq C < \infty. \tag{3.1.2}$$

We consider the dynamics introduced in 2.1.1, but already rescaled diffusively

in time and space, and with a tension *slowly* changing in time:

$$dr_i = n^2(p_i - p_{i-1}) \, dt$$
$$dp_i = n^2(V'(r_{i+1}) - V'(r_i)) \, dt - n^2\gamma p_i \, dt - n\sqrt{2\gamma\beta^{-1}}dw_i, \qquad i = 1, \ldots, n-1,$$
$$dp_n = n^2(\bar{\tau}(t) - V'(r_n)) \, dt - n^2\gamma p_n \, dt - n\sqrt{2\gamma\beta^{-1}}dw_n$$

$$(3.1.3)$$

Here $\{w_i(t)\}_i$ are n-independent standard Wiener processes, $\gamma > 0$ is a parameter of intensity of the interaction with the heat bath, p_0 is set identically to 0. The external force $\bar{\tau}(t)$ changes at the macroscopic time scale.

The generator of this diffusion is given by

$$\mathcal{L}_n^{\bar{\tau}(t)} := n^2 A_n^{\bar{\tau}(t)} + n^2\gamma S_n. \qquad (3.1.4)$$

Here the Liouville operator A_n^τ is given by

$$\begin{aligned} A_n^\tau &= \sum_{i=1}^n (p_i - p_{i-1})\frac{\partial}{\partial r_i} + \sum_{i=1}^{n-1} (V'(r_{i+1}) - V'(r_i))\frac{\partial}{\partial p_i} \\ &\quad + (\tau - V'(r_n))\frac{\partial}{\partial p_n}, \end{aligned} \qquad (3.1.5)$$

while

$$S = \sum_{i=1}^n \left(\beta^{-1}\partial_{p_i}^2 - p_i\partial_{p_i}\right) \qquad (3.1.6)$$

Notice that

$$Sp_i = -p_i, \qquad Sp_i^2 = \beta^{-1} - p_i^2 \qquad (3.1.7)$$

For $\tilde{\tau}(t) = \tau$ constant, we have seen already that the canonical measure $\mu_{\tau,\beta}^{c,m}$ defined by

$$d\mu_{\tau,\beta}^{c,n} = \prod_{j=1}^n e^{-\beta(\mathcal{E}_j - \tau r_j) - \mathcal{G}(\tau,\beta)} dr_j dp_j \qquad (3.1.8)$$

is stationary for this dynamics, where

$$G(\tau,\beta) = \log\left[\sqrt{2\pi\beta^{-1}}\int e^{-\beta(V(r)-\tau r)}dr\right]. \qquad (3.1.9)$$

We will need also to consider local Gibbs measure (inhomogeneous product), corresponding to profiles of tension $\{\tau(x), x \in [0,1]\}$:

$$d\mu_{\tau(\cdot),\beta}^n = \prod_{i=1}^n e^{-\beta(\mathcal{E}_i - \tau(i/n)r_i) - \mathcal{G}(\tau(i/n),\beta)} \, dr_i \, dp_i = g_{\tau(\cdot)}^n d\mu_{0,\beta}^{c,n} \qquad (3.1.10)$$

so that $g^n_{\tau(\cdot)}$ is the probability density (with respect to $\mu^n_{0,\beta}$) defined by

$$g^n_{\tau(\cdot)} = \prod_{i=1}^n e^{\beta\tau(i/n)r_i - \mathcal{G}(\tau(i/n),\beta) + \mathcal{G}(0,\beta)}.$$

Given an initial profile of tension $\tau(0,x)$, we assume that initial probability state is given by an absolutely continuous measure (with respect to the Lebesgue measure), whose density with respect to $d\mu^n_{0,\beta}$ is given by f^n_0, such that the relative entropy with respect to $\mu^n_{\tau(0,x),\beta}$

$$H_n(0) = \int f^n_0 \log\left(\frac{f^n_0}{g^n_{\tau(0,\cdot)}}\right) d\mu^{c,n}_{0,\beta} \tag{3.1.11}$$

satisfies

$$\lim_{n\to\infty} \frac{H_n(0)}{n} = 0 \tag{3.1.12}$$

This implies the following convergence in probability with respect to f^n_0:

$$\frac{1}{n}\sum_{i=1}^n G(i/n)r_i(0) \longrightarrow \int_0^1 G(x)\mathfrak{r}(\tau(0,x))\, dx \tag{3.1.13}$$

The macroscopic evolution for the stress will be given by

$$\begin{aligned}
&\partial_t r(t,x) = \gamma^{-1}\partial_x^2 \boldsymbol{\tau}(r(x,t)), \quad x\in[0,1]\\
&\partial_x r(t,0) = 0, \quad \boldsymbol{\tau}(r(t,1)) = \bar{\tau}(t), \quad t>0 \\
&\boldsymbol{\tau}(r(0,x)) = \tau(0,x), \quad x\in[0,1]
\end{aligned} \tag{3.1.14}$$

Observe that we do not require that $\tau(r(0,1)) = \bar{\tau}(0)$, so we can consider initial profiles of equilibrium with tension different than the applied $\bar{\tau}$.

In the following we use the notation $\tau(t,x) = \boldsymbol{\tau}(r(t,x))$, and $g^n_t = g^n_{\tau(t,\cdot)}$.

Let f^n_t the probability density, with respect to $\mu^n_{0,\beta}$, of the configuration of the system at time t, i.e. the solution of the forward equation:

$$\partial_t f^n_t = \mathcal{L}^{\bar{\tau}(t)*}_n f^n_t$$

where $\mathcal{L}^{\bar{\tau}(t)*}_n$ is the adjoint of $\mathcal{L}^{\bar{\tau}(t)}_n$ with respect to $\mu^n_{0,\beta}$, i.e.

$$\begin{aligned}
\mathcal{L}^{\bar{\tau}(t)*}_n &= n^2 A^{\bar{\tau}(t)*}_n + n^2\gamma S_n, \\
A^{\bar{\tau}(t)*}_n &= -A^{\bar{\tau}(t)}_n + \beta\bar{\tau}(t)p_n.
\end{aligned}$$

The main result is the following

Theorem 3.1.1.
$$\lim_{n \to \infty} \frac{H_n(t)}{n} = 0 \tag{3.1.15}$$

where

$$H_n(t) = \int f_t^n \log\left(\frac{f_t^n}{g_t^n}\right) \, d\mu_{0,\beta}^n \tag{3.1.16}$$

This proves the following hydrodynamic limit result:

$$\frac{1}{n} \sum_{i=1}^{n} G(i/n) r_i(t) \longrightarrow \int_0^1 G(x)\mathfrak{r}(t,x)) \, dx \tag{3.1.17}$$

where $\mathfrak{r}(t,x)$ is the solution of (3.1.14).

A schetch of the proof is postponed to section 3.4.

3.2   Work and Microscopic Heat

In the following we consider $\bar{\tau}(t)$ as a piecewise smooth bounded function such that $\bar{\tau}(0) = \tau_0$ and $\bar{\tau}(t) = \tau_1$ for $t \geq t_1$.

The microscopic total lenght is defined by $q_n = \sum_i r_i$, the position of the last particle. To connect it to the macroscopic space scale we have to divide it by n, so se define

$$\mathcal{L}_n(t) = \frac{q_n(t)}{n} = \frac{1}{n} \sum_{i=1}^{n} r_i(t). \tag{3.2.1}$$

The time evolution in the scale considered is given by

$$\mathcal{L}_n(t) - \mathcal{L}_n(0) = \int_0^t np_n(s) \, ds. \tag{3.2.2}$$

If we start with the equilibrium distribution with length r_0, the law of large numbers guarantees that

$$\mathcal{L}_n(0) \xrightarrow[n \to \infty]{} r_0, \tag{3.2.3}$$

in probability.

By theorem 3.1.1, we also have the convergence at time t:

$$\mathcal{L}_n(t) \xrightarrow[n \to \infty]{} L(t) \xrightarrow[t \to \infty]{} r_1 = \mathfrak{r}(\tau_1), \tag{3.2.4}$$

where $L(t)$ is defined by (1.6.25). notice that in (3.2.2) while $np_n(s)$ fluctuates wildly as $n \to \infty$, its time integral is perfectly convergent and in fact converges to a deterministic quantity.

The microscopic work done up to time t by the force $\bar{\tau}$ is given by

$$\mathcal{W}_n(t) = \int_0^t \bar{\tau}(s)d\mathcal{L}_n(s) = \int_0^t \bar{\tau}(s)np_n(s)ds \tag{3.2.5}$$

We adopt here the convention that positive work means energy increases in the system. Notice that $\mathcal{W}_n(t)$ defines the actual microscopic work divided by n.

It is a standard exercise to show that, since $\bar{\tau}(t)$ and $L(t)$ are piecewise smooth functions of t, by (3.2.4) it follows that

$$\mathcal{W}_n(t) \xrightarrow[n\to\infty]{} W(t) = \int_0^t \bar{\tau}(s)dL(s) \tag{3.2.6}$$

given by (1.6.26).

Microscopically the (internal) energy of the system is defined by

$$U_n = \frac{1}{n}\sum_i \mathcal{E}_i \tag{3.2.7}$$

Energy evolves in time as

$$U_n(t) - U_n(0) = \mathcal{W}_n(t) + \mathcal{Q}_n(t)$$
$$\mathcal{Q}_n(t) = -\gamma \int_0^t n\sum_{i=1}^n \left(p_i^2(s) - T\right) ds + M_n(t) \tag{3.2.8}$$

where $\mathcal{Q}_n$ is the energy exchanged with the heat bath, what we call *heat*, and $M_n(t)$ is a martigale with quadratic variation given by

$$2\gamma\beta^{-1}\sum_{i=1}^n \int_0^t p_i(s)^2 ds$$

In the continuous noise model this is given explicitely by

$$M_n(t) = \sqrt{2\gamma\beta^{-1}}\sum_{i=1}^n \int_0^t p_i(s)dw_i(s)$$

The law of large numbers for the initial distribution gives

$$U_n(0) \xrightarrow[n\to\infty]{} U(\beta, \tau_0)$$

in probability. By the hydrodynamic limit, we have that

$$U_n(t) \xrightarrow[n\to\infty]{} \int_0^1 U(\beta, \tau(t,x)) \, dx \xrightarrow[t\to\infty]{} U(\beta, \tau_1). \tag{3.2.9}$$

Assuming (3.2.9), we have that $Q_n(t)$ converges, as $n \to \infty$, to the deterministic

$$Q(t) = \int_0^1 [U(\beta, \tau(t, x)) - U(\beta, \tau_0)] \ dx - W(t) \tag{3.2.10}$$

and as $t \to \infty$:

$$Q = U(\beta, \tau_1) - U(\beta, \tau_0) - W, \qquad \text{(first principle)}. \tag{3.2.11}$$

Recalling that the free energy is equal to $F = U - \beta^{-1}S$, then we can compute the variation of the entropy S as

$$\beta^{-1}(S_1 - S_0) = -(F_1 - F_0) + W + Q \tag{3.2.12}$$

or also that

$$Q = \beta^{-1}(S_1 - S_0) - \gamma^{-1} \int_0^\infty dt \int_0^1 dx \, (\partial_x \tau(t, x))^2 \tag{3.2.13}$$

In the quasi static limit, we have seen that $F_1 - F_0 = W$, and consequently $\beta Q = S_1 - S_0$, in accord to what thermodynamics prescribe for quasistatic transformations.

3.3   Quasi-static hydrodynamic limit

In the previous section the tension τ changes in a time scale like $t = s/n^2$, where s is the microscopic time scale. This is the same time scale the system needs to relax the elongation to equilibrium, and this is why we obtain an irreversible transformations governed by the diffusive Equation 3.1.14. In order to obtain the quasistatic reversible transformation, we need to change the tension in a slower time scale $t = s/n^{2+\alpha}$, for some $\alpha > 0$. Consequently ion order to see an evolution of the elongation we need to speed up time by a factor $n^{2+\alpha}$, i.e. to consider the equations:

$$dr_i = n^{2+\alpha}(p_i - p_{i-1}) \ dt$$
$$dp_i = n^{2+\alpha}(V'(r_{i+1}) - V'(r_i)) \ dt - n^{2+\alpha}\gamma p_i \ dt - n^{\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_i, \qquad i = 1, \ldots, n-1,$$
$$dp_n = n^{2+\alpha}(\bar{\tau}(t) - V'(r_n)) \ dt - n^{2+\alpha}\gamma p_n \ dt - n^{\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_n$$

$$\tag{3.3.1}$$

In this time scale it can be proven the following quasistatic limit [2]:

$$\frac{1}{n}\sum_{i=1}^n G(i/n)V'(r_i(t)) \longrightarrow \bar{\tau}(t) \int_0^1 G(x) \ dx \tag{3.3.2}$$

in probability, for any test function $G : [0,1] \to \mathbb{R}$. In fact a stronger results of quasi-static equilibrium is true: Let $\varphi(r_1, p_1, \ldots, r_k, p_k)$ a local function of the configurations, and $\theta_i \varphi = \varphi(r_{i+1}, p_{i+1}, \ldots, r_{i+k}, p_{i+k})$ its translation (well defined for $i + k << n$). Then, always in probability,

$$\frac{1}{n} \sum_{i=1}^{n-k} G(i/n) \theta_i \varphi(t) \xrightarrow[n \to \infty]{} \hat{\varphi}(\bar{\tau}(t), \beta) \int_0^1 G(x) \, dx \qquad (3.3.3)$$

where $\hat{\varphi}(\tau, \beta) = \int \varphi \, d\mu^c_{\tau, \beta}$.

We cvan now repeat all the consideration made before, but without the need to let $t \to \infty$. Recall that we have defined

$$U_n := \frac{1}{n} \sum_{i=1}^{n} \left(\frac{p_i^2}{2} + V(r_i) \right) \qquad (3.3.4)$$

then internal energy evolves as:

$$U_n(t) - U_n(0) = \mathcal{W}_n(t) + Q_n(t)$$

where

$$\mathcal{W}_n(t) = n^{1+\alpha} \int_0^t \bar{\tau}(s) p_n(s) ds = \int_0^t \bar{\tau}(s) \frac{dq_n(s)}{n}$$

is the (normalized) work done by the force $\bar{\tau}(s)$ up to time t, while

$$Q_n(t) = \gamma \, n^{1+\alpha} \sum_{j=1}^{n} \int_0^t ds \left(p_j^2(s) - \beta_j^{-1} \right) + n^{\alpha/2} \sum_{j=1}^{n} \sqrt{2\gamma \beta_j^{-1}} \int_0^t p_j(s) dw_i(s). \quad (3.3.5)$$

is the total flux of energy between the system and the heat bath (divided by n). As a consequence of (3.3.3) we have that

$$\lim_{n \to \infty} \mathcal{W}_n(t) = \int_0^t \bar{\tau}(s) d\mathcal{L}(s) := \mathcal{W}(t)$$

where $\mathcal{L}(t) = \int_0^1 r(x,t) dx = \mathrm{r}(\tilde{\tau}(\mathrm{t}), \beta)$, the total macroscopic length at time t. While for the energy difference we expect that

$$\lim_{n \to \infty} (U_n(t) - U_n(0)) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) \qquad (3.3.6)$$

where $u(\tau, \beta)$ is the average energy for $\mu_{\beta, \tau}$, i.e.

$$u(\tau, \beta) = \int \mathcal{E}_1 d\mu^1_{\tau, \beta} = \frac{1}{2\beta} + \int V(r) e^{-\beta(V(r) - \tau r) - \tilde{\mathcal{G}}(\tau, \beta)} dr$$

By (3.3.3) we have

$$Q_n(t) \xrightarrow[n\to\infty]{} Q(t) \tag{3.3.7}$$

where $Q(t)$ is deterministic and satisfy the relation

$$Q(t) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) - \mathcal{W}(t). \tag{3.3.8}$$

which is the first principle of thermodynamics for quasistatic transformations.

Free energy and Clausius identity

Recall that in this case $\mathcal{L}(t) = \mathrm{r}(\tilde{\tau}(\mathrm{t}), \beta)$, and the corresponding Free Energy:

$$\widetilde{\mathcal{F}}(t) = \mathcal{F}(\mathcal{L}(t), \beta) \tag{3.3.9}$$

Then

$$\frac{d}{dt}\widetilde{\mathcal{F}}(t) = \tilde{\tau}(t)\frac{d}{dt}\mathcal{L}(t)$$

A straightforward calculation gives

$$\widetilde{\mathcal{F}}(t) - \widetilde{\mathcal{F}}(0) = \int_0^t ds\, \bar{\tau}(s)\, \frac{d}{ds}\mathcal{L}(s) = \int_0^t \bar{\tau}(s)d\mathcal{L}(s) = \mathcal{W}(t) \tag{3.3.10}$$

i.e. Clausius equality for the free energy.

Equivalently, by using the thermodynamic relation $\mathcal{F} = u - \beta^{-1}S$, we have

$$\beta^{-1}\left(S(\mathcal{L}(t), u(t)) - S(\mathcal{L}(0), u(0))\right) = Q(t) \tag{3.3.11}$$

I.e. $\dot{S} = \beta\dot{Q}$, the usual Clausius definition for the thermodynamic entropy in quasistatic isothermal thermodynamic trasformations.

3.4   Proof of the hydrodynamic limit

In the following we use the notation $\tau_x(t, x) = \partial_x\tau(t, x)$ and $\tau_{xx}(t, x) = \partial_{xx}\tau(t, x)$. For simplicity we do the calculations with the Langevin heat bath (3.1.6).

Define the modified local Gibbs density

$$\tilde{g}_t^n = e^{\frac{\beta}{\gamma}\sum_{i=1}^n[\frac{1}{n}\tau_x(t,i/n) + \frac{1}{2n^2}\tau_{xx}(t,i/n)]p_i}\, g_t^n\, Z_{n,t}^{-1} \tag{3.4.1}$$

where $Z_{n,t}$ is a normalization factor. Then define the corresponding relative entropy

$$\tilde{H}_n(t) = \int f_t^n \log\left(\frac{f_t^n}{\tilde{g}_t^n}\right)\, d\mu_{0,\beta}^n. \tag{3.4.2}$$

It is easy to see that $\lim_{n\to\infty} n^{-1}\left(\tilde{H}_n(t) - H_n(t)\right) = 0$.

Computing the time derivative

$$\frac{d}{dt}\tilde{H}_n(t) = \int f_t^n \mathcal{L}_n^{\tilde{\tau}(t)}\left(\log \frac{f_t^n}{\tilde{g}_{\tau(t,\cdot)}^n}\right) d\mu_{0,\beta} - \int f_t^n \partial_t \log \tilde{g}_{\tau(t,\cdot)}^n \, d\mu_{0,\beta}^n \qquad (3.4.3)$$

Then we use the inequality

$$\mathcal{L}_n^{\tilde{\tau}(t)} \log h \leq \frac{\mathcal{L}_n^{\tilde{\tau}(t)} h}{h}$$

we obtain

$$\frac{d}{dt}\tilde{H}_n(t) \leq \int f_t^n \frac{\left[\mathcal{L}_n^{\tilde{\tau}(t)*} - \partial_t\right]\tilde{g}_t^n}{\tilde{g}_t^n} \, d\mu_{0,\beta}^n$$

By explicit calculation

$$n^2 \frac{\mathcal{A}_n^{\bar{\tau}(t)*}\tilde{g}_t^n}{\tilde{g}_t^n} = -n^2 \mathcal{A}_n^{\bar{\tau}(t)} \log \tilde{g}_t^n + n^2\beta\bar{\tau}(t)p_n$$

$$= -n^2 \sum_{i=1}^{n} \beta\tau(i/n)\mathcal{A}_n^{\bar{\tau}(t)}r_i - \sum_{i=1}^{n} \frac{\beta}{\gamma}\left(n\tau_x(i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)\mathcal{A}_n^{\bar{\tau}(t)}p_i + n^2\beta\bar{\tau}(t)p_n$$

$$= -n^2 \sum_{i=1}^{n} \beta\tau(i/n)(p_i - p_{i-1}) - \sum_{i=1}^{n-1} \beta\left(n\tau_x(i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)(V'(r_{i+1}) - V'(r_i))$$

$$\quad - \beta\left(n\tau_x(1) + \frac{1}{2}\tau_{xx}(1)\right)(\bar{\tau}(t) - V'(r_n)) + n^2\beta\bar{\tau}(t)p_n$$

$$= -n^2 \sum_{i=1}^{n-1} \beta(\tau(i/n) - \tau((i+1)/n))p_i - \sum_{i=1}^{n-1} \frac{\beta}{\gamma}\left(n\tau_x(i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)(V'(r_{i+1}) - V'(r_i))$$

$$\quad - \frac{\beta}{\gamma}\left(n\tau_x(1) + \frac{1}{2}\tau_{xx}(1)\right)(\bar{\tau}(t) - V'(r_n))$$

$$= \beta \sum_{i} \left\{\left(n\tau_x(t,i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)p_i + \frac{1}{\gamma}\tau_{xx}(i/n)V'(r_i) - \frac{n}{\gamma}\tau_x(1)\bar{\tau}(t)\right\} + o(n)$$

while

$$n^2\gamma\frac{\mathcal{S}_n\tilde{g}_t^n}{\tilde{g}_t^n} = n^2\frac{\beta}{\gamma}\sum_{i=1}^{n}\left(\frac{1}{n}\tau_x(i/n) + \frac{1}{2n^2}\tau_{xx}(i/n)\right)^2 - \beta\sum_{i=1}^{n}\left(n\tau_x(i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)p_i$$

$$= \frac{\beta}{\gamma}\sum_{i=1}^{n}\tau_x(i/n)^2 - \beta\sum_{i=1}^{n}\left(n\tau_x(i/n) + \frac{1}{2}\tau_{xx}(i/n)\right)p_i + o(n)$$

Then observe that

$$\sum_{i=1}^{n} \tau_x(i/n)^2 - n\tau_x(1)\bar{\tau}(t) = \sum_{i=1}^{n} \tau_x(i/n)^2 - n\tau_x(1)\tau(t,1)$$

$$= -\sum_{i=1}^{n} \tau_{xx}(i/n)\tau(i/n) + o(n)$$

So we have obtained that

$$\frac{\mathcal{L}_n^{\bar{\tau}(t)*} \tilde{g}_t^n}{\tilde{g}_t^n} = \frac{\beta}{\gamma} \sum_{i=1}^{n} \tau_{xx}(t,i/n) \left[V'(r_i) - \tau(t,i/n)\right] + o(n)$$

while

$$\partial_t \log \tilde{g}_{\tau(t,\cdot)}^n = \beta \sum_i \tau_t(t,i/n)(r_i - r(t,i/n)) + O(1).$$

and since

$$\tau_t(t,x) = \frac{d\boldsymbol{\tau}}{d\boldsymbol{r}} \partial_t r(t,x) = \frac{d\boldsymbol{\tau}}{d\boldsymbol{r}} \tau_{xx}(t,x),$$

we have obtained

$$\frac{\left[\mathcal{L}_n^{\bar{\tau}(t)*} - \partial_t\right] \tilde{g}_t^n}{\tilde{g}_t^n}$$

$$= \frac{\beta}{\gamma} \sum_{i=1}^{n} \tau_{xx}(t,i/n) \left([V'(r_i) - \tau(t,i/n)] - \frac{d\boldsymbol{\tau}}{d\boldsymbol{r}}(r(t,i/n))[(r_i - r(t,i/n)]\right) + o(n)$$

where the $o(n)$ is intended to be small after all integratin made (one has to be careful since we are dealing with unbounded quantities).

The rest of the proof follows by the standard arguments of the relative entropy method (cf. [7–9, 11]).

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