From Dynamics to Thermodynamics

Stefano Olla

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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 (also called *laws*), and the objects of the thermodynamics are those systems that satisfy these laws. More precisely we should look at this principles as requirements on the system, like the existence of multiple equilibrium states[1].

This is still quite vague. In fact thermodynamics describe certain possible transformations 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 the macroscopic space-time scales required in order to obtain the transformations described by the principles of thermodynamics[2]. Mathematically space-time macroscopic scale means we will perform a scaling limit.

I find more useful to explain the main ideas in the most simple system: a one dimensional bar, or an elastic, whose equilibrium thermodynamic states are parametrized by the *tension* and the *temperature* (intensive parameters determined by exterior *agents*), 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 necessary minimal thermodynamic concepts. There exist

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[1] In this sense we talk about *Equilibrium Thermodynamics*, even though, when performing thermodynamic transformations, in order to change one equilibrium state to another, we need to push the system out of equilibrium. This point will be discussed later extensively.

[2] In other words we look at Thermodynamics as an *emergent* theory at macroscopic scales from the microscopic dynamics.

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*[3]:

> *If a wire A, under the tension $\boldsymbol{\tau}$, remains in equilibrium when isolated and placed in contact 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.

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[3] 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 first understoof by Mayer in 1842, but 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 [16].

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 [16] 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. Even worst, it does not even imply a complete order between states at different temperatures. The only way to establish a complete order and identify θ as a real parameter is to use a reference material[4] whose equilibrium states are uniquely characterised by the length $\mathcal{L}$ and the tension $\boldsymbol{\tau}$. Then one can choose any arbitrary real valued function $\theta_{\text{ref}}(\mathcal{L}, \boldsymbol{\tau})$ strictly monotone in $\mathcal{L}$ and in $\boldsymbol{\tau}$, and call it temperature of the reference material[5]. Then, by the zero principle, we can use this reference material as a *thermometer* in order to define the temperature of all other systems (that satisfy the 0-principle).

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 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 imply much more than the definition of the empirical temperature. The 0-Law says that we know all the equilibrium states of the system, and that they are **all** parametrized by the tension and temperature, or by tension and volume etc. It means that there is correspondingly only one equilibrium state[6]. 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 in our system that there are only two *relevant conserved quantities* in the infinite dynamics: elongation and the energy. Notice that, as usual in thermodynamics, the principle is not saying anything about the time scale in which the system is reaching the equilibrum state if perturbed, that will be a very important issue in rthe connection to microscopic dynamics.

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[4] In classical treatment one takes the ideal gas, where $\theta = \boldsymbol{\tau}\ell$.

[5] This is a very empirical and certainly unsatisfactory definition of temperature, that will be fixed later by the introduction of the *absolute temperature* after the second principle

[6] We are excluding, in these one dimensional systems, the existence of phase transitions that will slightly complicate the issue.

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*[7], 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

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

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[8].

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.

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

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[8] 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. We are also assuming that for enough regular behavior of $\tilde{\tau}(t)$, the length $\mathcal{L}(s)$ is enough regular so that (1.2.1) is well defined

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 [9] 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[10].

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 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** [11].

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[9] 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.

[10] 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.

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

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** (3.1.13) **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 [12].

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.).

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 [16], *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

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[12] Already O.E.Lanford III, in his lectures on *Mathematical Statistical Mechanics* [9], 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'.

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 $\text{đ}W$. 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 $\oint \text{đ}W \neq 0$ (equal to the area inside the path), and represent the work done on the system by the external force (tension).

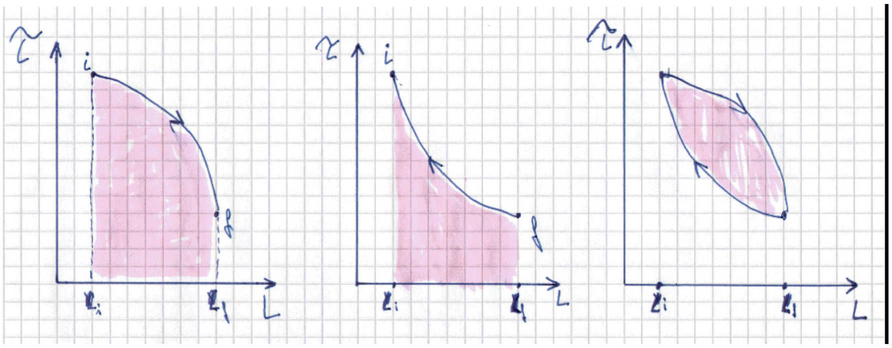
During a quasi-static thermodynamic infinitesimal transformation, this energy is modified by the work $\text{đ}W$ and, since dU has to be an exact differential, by some other (not exact) differential form $\text{đ}Q$ called *heat exchange*:

$$dU = \tau d\mathcal{L} + \text{đ}Q \tag{1.3.8}$$

1.3.1 Thermodynamic transformations and cycles

We can compute the changes 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

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

  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 $\not{d}W = 0$, no work if performed to or by the system, and

$$\not{d}Q = dU \tag{1.3.13}$$

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

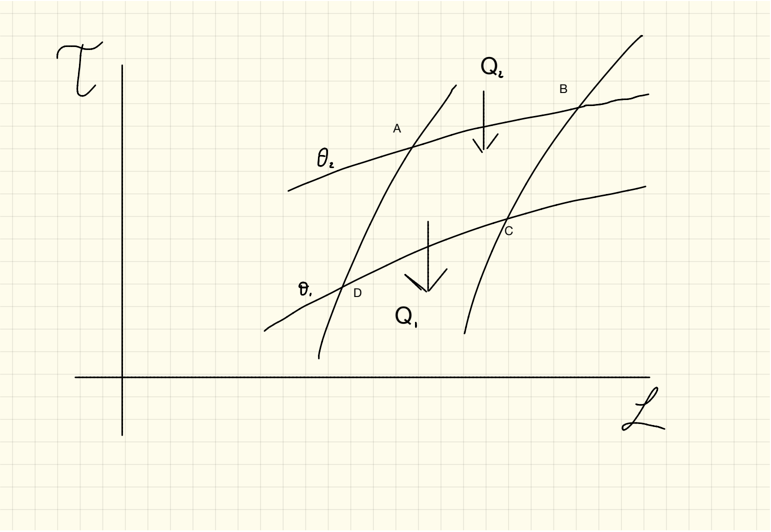
Special Example: The harmonic (linear) system.

We will encounter a special (ideal) system for which $\tau(L,\theta) = \bar{\tau}L$ where $\bar{\tau}$ is a positive constant. Then $U(L,\theta) = \frac{\bar{\tau}}{2}L^2 + \theta$. In this case all isothermal and adiabatic lines in the (L,τ) plane degenerate trivially in a unique straight line $\tau = \bar{\tau}L$. 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:

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

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 $\eta < 1$[13].

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 [14]:

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[13] 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 $Q_1 < Q_2$.

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

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

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*.

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

$$N' Q_1' \geq N Q_1 \tag{1.4.8}$$

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 (1.4.5) 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[15]. 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

$$0 < \frac{Q_2}{Q_2'} - \frac{N_k'}{N_k} < \frac{1}{N_k' N_{k-1}'} \tag{1.4.10}$$

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. □

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[15] The following argument was suggested by Tomasz Komorowski

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 (1.6.36) : 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 (1.6.36) and (1.6.37),

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

and considering that θ_1 is arbitrary in this argument, this quantity does not depend on it and we obtain (1.6.36). □

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 $\frac{\text{đ}Q}{T}$, this means

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

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), (3.3.2) is actually valid for any cycle, i.e. any closed (peacewise smooth) curve on the state space. Consequently $\frac{\text{đ}Q}{T}$ is an exact form, i.e. the differential of a function S of the state of the system. This function is called Thermodynamic Entropy. [16]

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

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

i.e.

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

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

$$dU = \tau d\mathcal{L} + T dS \tag{1.4.17}$$

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

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[16] 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.

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

$$Q \leq T\left(S(B) - S(A)\right). \tag{1.4.18}$$

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.

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:

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

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

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

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*

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

The choice to consider $\mathcal{G}$ as a function of the inverse temperature T^{-1}, simplify notation and connection with the statistical mechanics. We will use the variable $\beta = T^{-1}$.

Exercice:

$$S(U, \mathcal{L}) = \inf_{\boldsymbol{\tau},\beta} \{ \beta U - \beta \boldsymbol{\tau} \mathcal{L} + \mathcal{G}(\boldsymbol{\tau}, \beta) \} \tag{1.6.4}$$

The differential forms $đQ = TdS = \beta^{-1} dS$ is called *heating*, and $\boldsymbol{\tau} d\mathcal{L}$ *work*. Since $dS = -\beta \boldsymbol{\tau} d\mathcal{L} + \beta dU$, it implies that

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

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

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

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

$$Q \leq \beta^{-1} \left[S(B) - S(A)\right] \tag{1.6.7}$$

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

$$-W \leq -[U(B) - U(A)] + \beta^{-1}[S(B) - S(A)].$$

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* $F(\mathcal{L}, \beta)$ as

$$F(\mathcal{L}, \beta) = \inf_{U>0} \left\{U - \beta^{-1} S(U, \mathcal{L})\right\} = \sup_{\boldsymbol{\tau}} \left\{\boldsymbol{\tau}\mathcal{L} - \beta^{-1}\mathcal{G}(\boldsymbol{\tau}, \beta)\right\} \tag{1.6.8}$$

From (1.6.8) we also obtain

$$\partial_{\mathcal{L}} F = \boldsymbol{\tau} \ . \tag{1.6.9}$$

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

$$W \geq F(B) - F(A) = \Delta F \tag{1.6.10}$$

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.

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.

The following subsection 1.6.1 will not be treated this year. It belongs to previous versions. This year we will consider only homogeneous systems and quasistatic trasformations.

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

$$\begin{aligned} S(M_1, U_1, \mathcal{L}_1) + S(M_2, U_2, \mathcal{L}_2) &\leq 2S\left(\frac{M_1 + M_2}{2}, \frac{U_1 + U_2}{2}, \frac{\mathcal{L}_1 + \mathcal{L}_2}{2}\right) \\ &= S(M_1 + M_2, U_1 + U_2, \mathcal{L}_1 + \mathcal{L}_2) \end{aligned} \tag{1.6.11}$$

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[17]

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

$$\mathcal{L}(x) = \int_0^x r(x')dx' \tag{1.6.12}$$

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):

$$\mathcal{L}_{tot} = \int_0^M r(x)dx, \quad U_{tot} = \int_0^M U(x)dx, \quad S_{tot} = \int_0^M S(1, U(x), r(x))dx. \tag{1.6.13}$$

By concavity of S:

$$S_{tot} \leq MS(1, M^{-1}U_{tot}, M^{-1}\mathcal{L}_{tot}) = S(M, U_{tot}, \mathcal{L}_{tot}) \tag{1.6.14}$$

Usual thermodynamics does not worry about time scales where the thermodynamic processes happens. But in the extended thermodynamics we can consider

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[17] 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.

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:

$$\partial_t S(U(x,t), r(x,t)) = \frac{1}{T}\left(\dot{U} - \boldsymbol{\tau}\dot{r}\right) \tag{1.6.15}$$

We can define the right hand side of (5.2.6) as the instantaneous heat flux. This is well defined only for *regular* (smooth) evolutions.

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

$$\begin{aligned} \partial_t r &= \partial_x \pi \\ \partial_t \pi &= \partial_x \boldsymbol{\tau} \\ \partial_t U &= \partial_x(\boldsymbol{\tau}\pi) - \pi\partial_x\boldsymbol{\tau} = \boldsymbol{\tau}\partial_x\pi \end{aligned} \tag{1.6.16}$$

These should be implemented by the boundary conditions:

$$\pi(t,0) = 0, \ \boldsymbol{\tau}(U(t,1), r(t,1)) = \bar{\tau}(t) \tag{1.6.17}$$

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:

$$\partial_t\mathcal{E} = \partial_x(\boldsymbol{\tau}\pi) \tag{1.6.18}$$

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[18]. 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 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 $\tilde{}(t)$ 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:

$$\partial_t r(x,t) = \partial_x^2 \boldsymbol{\tau}(r(x,t), T) \tag{1.6.19}$$

We add the boundary conditions

$$\begin{aligned} \partial_x r(0,t) &= 0 \\ \boldsymbol{\tau}(r(1,t), T) &= \tilde{\tau}(t) \end{aligned} \tag{1.6.20}$$

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

$$\mathcal{F}(t) = \int_0^1 F(r(x,t), T)\, dx \tag{1.6.21}$$

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

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

$$\lim_{t\to\infty} \boldsymbol{\tau}(r(t,x),T) \ = \ \tau_1, \qquad \forall x \in [0,1] \tag{1.6.22}$$

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

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

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

$$\begin{aligned} W(t) = \int_0^t \tilde{\tau}(s) dL(s) = \int_0^t ds\ \tilde{\tau}(s) \ \int_0^1 dx\ \partial_x^2 \boldsymbol{\tau}(r(s,x),T) \\ = \int_0^t \tilde{\tau}(s) \partial_x \boldsymbol{\tau}(r(s,1),T) ds \end{aligned} \tag{1.6.24}$$

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

$$\mathcal{F}(t) = \int_0^1 F(r(t,x),T)\, dx. \tag{1.6.25}$$

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 (1.6.22) we have $\mathcal{F}(t) \to F(\tau_1, T)$, and we conclude that

$$F(\tau_1, T) - F(\tau_0, T) = W - \int_0^{+\infty} ds \int_0^1 \left(\partial_x \boldsymbol{\tau}(r(s,x),T)\right)^2\, dx \tag{1.6.26}$$

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 (1.6.24) for $t \to \infty$:

$$W = \int_0^\infty \tilde{\tau}(s) dL(s) = \int_0^\infty \tilde{\tau}(s) \partial_x \boldsymbol{\tau}(r(s,1),T) ds \tag{1.6.27}$$

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 (1.6.26) 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 surprizing 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

$$\partial_t r_\varepsilon(t,x) = \partial_x^2 \boldsymbol{\tau}(r_\varepsilon(t,x),T) \tag{1.6.28}$$

with boundary conditions

$$\begin{aligned} &\partial_x r_\varepsilon(t,0) = 0 \\ &\boldsymbol{\tau}(r_\varepsilon(t,1),T) = \tilde{\tau}(\varepsilon t) \end{aligned} \tag{1.6.29}$$

Then (1.6.26) became

$$F(r_1,T) - F(r_0,T) = W_\varepsilon - \int_0^\infty ds \int_0^1 \left(\partial_x \boldsymbol{\tau}(r_\varepsilon(s,x),T)\right)^2 \, dx \tag{1.6.30}$$

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

$$0 < C_1 \le \tilde{\tau}'(r) \le C_2 < \infty \tag{1.6.31}$$

which is a natural assumption on the strict diffusivity of the equation (1.6.19).

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

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

$$\lim_{\varepsilon\to 0} \int_0^\infty ds \int_0^1 \left(\partial_x \boldsymbol{\tau}(r_\varepsilon(s,x))\right)^2 \, dx = 0 \tag{1.6.32}$$

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

$$\partial_{\mathfrak{t}} \tilde{r}_\varepsilon(\mathfrak{t},x) = \varepsilon^{-1} \partial_x^2 \boldsymbol{\tau}(\tilde{r}_\varepsilon(\mathfrak{t},x)) \tag{1.6.33}$$

with boundary conditions

$$\begin{aligned} &\partial_x r_\varepsilon(\mathfrak{t},0) = 0 \\ &\boldsymbol{\tau}(r_\varepsilon(\mathfrak{t},1)) = \tilde{\tau}(\mathfrak{t}) \end{aligned} \tag{1.6.34}$$

$$
\begin{aligned}
&\frac{1}{2}\int_0^1 \left(\tilde r_\varepsilon(\mathfrak{t},x)-\mathfrak{r}[\tilde\tau(\mathfrak{t})]\right)^2 dx\\
&\quad=\int_0^{\mathfrak{t}} ds\int_0^1 dx\ \left(\tilde r_\varepsilon(s,x)-\mathfrak{r}(\tilde\tau(s))\right)\left(\varepsilon^{-1}\partial_x^2\boldsymbol{\tau}[\tilde r_\varepsilon(s,x)]-\frac{d}{ds}\mathfrak{r}[\tilde\tau(s)]\right)\\
&\quad=-\,\varepsilon^{-1}\int_0^{\mathfrak{t}} ds\int_0^1 dx\ \left(\partial_x\tilde r_\varepsilon(s,x)\right)^2\frac{d\boldsymbol{\tau}}{dr}\left[\tilde r_\varepsilon(s,x)\right]\\
&\qquad-\int_0^t ds\frac{d\mathfrak{r}}{d\tau}(\tilde\tau(s))\tilde\tau'(s)\int_0^1 dx\ \left(\tilde r_\varepsilon(s,x)-\tilde r_\varepsilon(s,1)\right)
\end{aligned}
\tag{1.6.35}
$$

Rewriting

$$
\begin{aligned}
&\left|\int_0^1 dx\ \left(\tilde r_\varepsilon(s,x)-\tilde r_\varepsilon(s,1)\right)\right|=\left|\int_0^1 dx\ \int_x^1 dy\ \partial_y\tilde r_\varepsilon(s,y)\right|\\
&\quad=\left|\int_0^1 dy\ y\partial_y\tilde r_\varepsilon(s,y)\right|\le\frac{\alpha}{2\varepsilon}\int_0^1 dx\ \left(\partial_x\tilde r_\varepsilon(s,x)\right)^2+\frac{\varepsilon}{6\alpha}
\end{aligned}
$$

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

$$
\frac{1}{2}\int_0^1 \left(\tilde r_\varepsilon(\mathfrak{t},x)-\mathfrak{r}[\tilde\tau(\mathfrak{t})]\right)^2 dx+\varepsilon^{-1}\left(C_--\frac{\alpha}{2C_-}\right)\int_0^{\mathfrak{t}} ds\int_0^1 dx\ \left(\partial_x\tilde r_\varepsilon(s,x)\right)^2\le\frac{\varepsilon t_1}{6\alpha C_-}
\tag{1.6.36}
$$

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

$$
\frac{1}{C_-}\int_0^1 \left(\tilde r_\varepsilon(\mathfrak{t},x)-\mathfrak{r}[\tilde\tau(t_1)]\right)^2 dx+\varepsilon^{-1}\int_0^{\mathfrak{t}} ds\int_0^1 dx\ \left(\partial_x\tilde r_\varepsilon(s,x)\right)^2\le\varepsilon\frac{t_1}{3C_-^4}
\tag{1.6.37}
$$

then we can take the limit as $\mathfrak{t}\to\infty$, the first term on the right hand side of (1.6.37) will disappear, and we obtain

$$
\varepsilon^{-1}\int_0^{+\infty} ds\int_0^1 dx\ \left(\partial_x\tilde r_\varepsilon(s,x)\right)^2\le\varepsilon\frac{t_1}{3C_-^4}
\tag{1.6.38}
$$

that implies (1.6.32). □

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

$$\lim_{\varepsilon\to 0}\int_0^1 \left(r_\varepsilon(t,x) - \mathfrak{r}[\tilde{\tau}(\varepsilon t)]\right)^2 dx = 0 \tag{1.6.39}$$

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

$$\Delta U = \Delta F + T\Delta S = W - \int_0^{+\infty} ds \int_0^1 dx\ \left(\partial_x \boldsymbol{\tau}(r(s,x),T)\right)^2 + T\Delta S \tag{1.6.40}$$

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 $Q = -\int_0^{+\infty} ds \int_0^1 dx\ \left(\partial_x r(s,x)\right)^2$, 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 [6], reprint of the notes of the course he gave at Columbia University in 1936.

The textbook of Zemansky [16] 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 [15] 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 [4] 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 (isobaric)

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 $j = 1, \dots m$. We denote with $q_j, j = 1, \dots, m$ 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

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

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 $\{p_j, r_j, j = 1, \dots, m\} \in \mathbb{R}^{2m}$, and energy function (Hamiltonian) defined on each configuration is given by

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

where

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

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:

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

Define

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

We will see soon that this function identify with the one introduced in the previous section 1.6 by (1.6.3). It is easy to see that, for any $\beta > 0$, the canonical measure $\mu^{c,m}_{\tau,\beta}$ defined by

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

is stationary for this dynamics.

The distribution $\mu^{c,m}_{\tau,\beta}$ 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 $\{r_1, \dots, r_m, p_1, \dots, p_m\}$ are independently distributed under this probability measure.

We have the following immediate relations:

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

and the average elongation and energy in the canonical measure:

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

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:

$$\begin{aligned} &\dot r_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1,\dots,m, \\ &dp_j(t) = (V'(r_{j+1}(t)) - V'(r_j(t)))\; dt - \gamma_j p_j \; dt + \sqrt{2\gamma_j\beta^{-1}}\; dw_j(t), \qquad j = 1,\dots,m-1, \\ &dp_m(t) = (\tau - V'(r_m(t)))\; dt - \gamma_m p_m \; dt + \sqrt{2\gamma_m\beta^{-1}}\; dw_m(t), \end{aligned} \tag{2.1.7}$$

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 $\mu^{c,m}_{\tau,\beta}$. 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:

$$\begin{aligned} &\dot r_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1,\dots,m, \\ &dp_j(t) = (V'(r_{j+1}(t)) - V'(r_j(t)))\; dt - (p_j(t^-) - \tilde p_{j,N_j(t)}) dN_j(t) \qquad i = 1,\dots,m-1, \\ &dp_m(t) = (\bar\tau(t) - V'(r_m))\; dt - (p_m(t^-) - \tilde p_{m,N_m(t)}) dN_m(t), \end{aligned} \tag{2.1.8}$$

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

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

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

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

Ovsreve that S is concave, since inf of linear functions.

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].

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):

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

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

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

where $đQ$ is the (non-exact) differential [3]

$$đQ = -\tau d\mathcal{L} + dU. \tag{2.2.8}$$

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

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

---

[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 $k = \frac{R}{N_A} = 1.38 \cdot 10^{-23} J/K$

[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 [8]. We still need some dynamical argument to indentify S with the Clausius entropy we have defined using Carnot cycles.

and we have

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

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

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

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 $(r_1, p_1, \dots, r_n, p_n)$ 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

$$\begin{aligned} &\int G(\hat{\mathbf{S}}_n) H(r_1, p_1, \dots, r_n, p_n)\, d\mu^{c,n}_{\tau_0,\beta_0}(r_1, p_1, \dots, r_n, p_n) \\ &= \int_{\mathbb{R}\times\mathbb{R}_+} d\mathbf{x}\, G(\mathbf{x}) f_n(\mathbf{x}) \int H(r_1, p_1, \dots, r_n, p_n)\, d\mu^{mc,n}_{\mathbf{x}}(r_1, p_1, \dots, r_n, p_n | \mathbf{x}) \end{aligned}$$

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*

$$\lim_{n\to\infty} \int F(r_1, p_1, \dots, r_k, p_k)\, d\mu_{\mathbf{x}}^{mc,n}(r_1, p_1, \dots, r_n, p_n) \\ = \int F(r_1, p_1, \dots, r_k, p_k)\, d\mu_{\tau,\beta}^{c,k}(r_1, p_1, \dots, r_k, p_k)$$

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*

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

Then

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

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* $y \in (0, 1)$,

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

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

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:

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

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

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

where F_j are local bounded functions.

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

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

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.

2.4 Comments on the literature

For the equivalence of ensembles [2].

Chapter 3

Quasi-Static Isothermal transformations

In this chapter we obtain a thermodynamic quasi static isothermal transformations from the space-time rescaling of the microscopic dynamics of the chain in contact with a heat bath at temperature β^{-1}, and with a slowly varying tension $\bar{\tau}(t)$, as defined in section 2.1.1. We consider the situation where the heat bath acts uniformly in the 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 at a diffusive space-time scale. Looking at a longer time scale, and changing the tension at this macroscopic scale we obtain a 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:

$$\begin{aligned}
dr_i &= n^{2+\alpha}(p_i - p_{i-1})\, dt \\
dp_i &= n^{2+\alpha}(V'(r_{i+1}) - V'(r_i))\, dt - n^{2+\alpha}\gamma p_i\, dt - n^{\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_i, \qquad i = 1, \dots, n-1, \\
dp_n &= n^{2+\alpha}(\bar\tau(t) - V'(r_n))\, dt - n^{2+\alpha}\gamma p_n\, dt - n^{\alpha/2}\sqrt{2\gamma\beta^{-1}}dw_n
\end{aligned} \tag{3.1.3}$$

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, and $\alpha > 0$. The case $\alpha = 0$ will be the natural diffusive space-time scaling where the volume elongation profile will converges to a diffusive equation citeollaisoth. Notice that the external force $\bar\tau(t)$ changes at the macroscopic time scale.

The generator of this diffusion is given by

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

Here the Liouville operator A_n^τ is given by

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

while

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

Notice that

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

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

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

is stationary for this dynamics, where

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

Given an evolution of the tension $\bar\tau(t)$ for $t \in [0,t]$, we start the system with the distribution given by $\mu_{\bar\tau(0),\beta}^{c,n}$. We want to prove that at time $t > 0$, the dristribution is very close to $\mu^{c,n}_{\bar\tau(t),\beta}$. Let $f^n_t(r_1,p_1,\dots,r_n,p_n)$ the density of the distribution at time t with respect to $\mu^{c,n}_{\bar\tau(t),\beta}$. This is the solution of the forward equation:

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

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

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

The relative entropy of the distribution at time t with respect to $\mu^{c,n}_{\bar\tau(t),\beta}$ is defined by

$$H_n(t) = \int f^n_t \log f^n_t \; d\mu^{c,n}_{\bar\tau(t),\beta}. \tag{3.1.10}$$

Clearly

$$H_n(0) = 0 \tag{3.1.11}$$

We prove now the following theorem that imply the quasi-static limit:

Theorem 3.1.1.

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

This implies the following convergence in probability:

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

where we denote $\bar r(t) = \mathfrak{r}(\beta,\bar\tau(t)) = (\partial_\tau \mathcal{G})(\beta,\bar\tau(t))$ is the equilibrium volume at temperature β^{-1} and tension $\bar\tau(t)$.

3.2 Proof

In the following C will denote a generic constant not depending on n that may change for one formula to another.

Taking time derivative of the relative entropy we get

$$\frac{d}{dt} H_n(t) = \int \left(\log f^n_t\right) \left(\mathcal{L}^{\bar\tau(t)*}_n f^n_t\right) g^n_{\bar\tau(t)} \prod_{j=1}^n dr_j dp_j - \int f^n_t \partial_t g^n_{\bar\tau(t)} \prod_{j=1}^n dr_j dp_j. \tag{3.2.1}$$

Since $\tau(t)$ are differentiable, we have

$$\partial_t g^n_{\bar\tau(t)} = \beta\bar\tau'(t)\sum_{j=1}^n \left(r_j - \bar r(t)\right)\; g^n_{\bar\tau(t)},$$

and (4.2.4) gives

$$\begin{aligned}\frac{d}{dt}H_n(t) = &-n^{2+\alpha}\gamma\beta^{-1}\int\sum_{i=1}^n \frac{(\partial_{p_i} f^n_t)^2}{f^n_t}\; d\mu^{c,n}_{\bar\tau(t),\beta}\\ &-\beta\bar\tau'(t)\int\sum_{i=1}^n \left(r_i - \bar r(t)\right) f^n_t\; d\mu^{c,n}_{\bar\tau(t),\beta}.\end{aligned}$$

Notice that this implies that

$$\int \frac{1}{n}\sum_{i=1}^n \left(r_i - \bar r(t)\right) f^n_t\; d\mu^{c,n}_{\bar\tau(t),\beta} \underset{n\to\infty}{\longrightarrow} 0 \tag{3.2.2}$$

is then a necessary and sufficient condition for the theorem.

By entropy inequality, for any $\lambda > 0$ small enough

$$\begin{aligned}\beta\bar\tau'(t)\int\sum_{i=1}^n \left(r_i - \bar r(t)\right) f^n_t\; d\mu^{c,n}_{\bar\tau(t),\beta} &\le \lambda^{-1}\log\int e^{\lambda\beta\bar\tau'(t)\sum_{i=1}^n (r_i - \bar r(t))}\; d\mu^{c,n}_{\bar\tau(t),\beta} + \lambda^{-1}H_n(t)\\ &= \frac{n}{\lambda}\left[\mathcal{G}(\beta,\tau(t)+\lambda\tau'(t)) - \mathcal{G}(\beta,\tau(t)) - \partial_\tau(\mathcal{G})(\beta,\tau(t))\lambda\tau'(t)\right] + \lambda^{-1}H_n(t)\\ &\le \lambda C n + \lambda^{-1}H_n(t),\end{aligned}$$

i.e.

$$\frac{d}{dt}H_n(t) \le \lambda^{-1}H_n(t) + \lambda C n,$$

and since $H_n(0) = 0$, it follows that $H_n(t) \le e^{t/\lambda}\lambda C t\; n$. This is not yet what we want to prove but it implies that

$$\int_0^T\int\sum_{i=1}^n \frac{(\partial_{p_i} f^n_t)^2}{f^n_t}\; d\mu^{c,n}_{\bar\tau(t),\beta}\; dt \le \frac{C}{n^{1+\alpha}}. \tag{3.2.3}$$

This gives only information on the distribution of the velocities. Let us assume that we have the same bound for the derivative with respect to the positions, i.e.

$$\int_0^T\int\sum_{i=1}^n \frac{(\partial_{q_i} f^n_t)^2}{f^n_t}\; d\mu^{c,n}_{\bar\tau(t),\beta}\; dt \le \frac{C}{n^{1+\alpha}}. \tag{3.2.4}$$

where $\partial_{q_i} = \partial_{r_i} - \partial_{r_{i+1}}$. We will prove that (3.2.4) follows from (3.2.3) in section xxx, using entropic hypocoercive bounds.

Now we prove that (3.2.4) implies (3.2.2), that concludes the proof.

In order to shorten notation, denote $\tilde{r}_i = r_i - \bar{r}(t)$. Divide the sum over blocks of length ℓ:

$$\frac{1}{n}\sum_{i=1}^{n} \tilde{r}_i = \frac{\ell}{n}\sum_{j=0}^{n/\ell} \bar{r}_{j,\ell}, \qquad \bar{r}_{j,\ell} = \frac{1}{\ell}\sum_{i=1}^{\ell} \tilde{r}_{j\ell+i}.$$

Denote the corresponding blocks $\Lambda_{j,\ell} = \{j\ell+1, \dots, (j+1)\ell\}, j = 0, \cdot, \frac{n}{l} - 1$, and by $f^n_{t,j,\ell}$ the projection of f^n_t on $\Lambda_{j,\ell}$. These are probability densities on $\mathbb{R}^{2\ell}$ with respect to $d\mu^{c,\ell}_{\bar{\tau}(t),\beta}$, that, by Jensen's inequality, satisfy the bound

$$\sum_{j=0}^{n/\ell-1} \int_0^T \int_{\mathbb{R}^{2\ell}} \sum_{i=1}^{\ell} \frac{(\partial_{q_i} f^n_{t,j,\ell})^2 + (\partial_{p_i} f^n_{t,j,\ell})^2}{f^n_{t,j,\ell}} \, d\mu^{c,\ell}_{\bar{\tau}(t),\beta} \, dt \le \frac{C}{n^{1+\alpha}}. \tag{3.2.5}$$

It can be shown that, for almost every $t \in [0,T]$, the sequence of probability mesures $\{f^n_{t,j,\ell} d\mu^{c,\ell}_{\bar{\tau}(t),\beta}\}_n$ on $\mathbb{R}^{2\ell}$ is compact, and any limit point has a density $f_{t,j,\ell}$ that is only a function of $\sum_{i=1}^{\ell} \tilde{r}_i$.

Furthermore, for the last block, we can show that $f^n_{t,n/\ell-1,\ell} d\mu^{c,\ell}_{\bar{\tau}(t),\beta}$, for $n \to \infty$ and $\ell \to \infty$ converges to $\mu_{\bar{\tau}(t),\beta}$, the Gibbs measure on the infinite system. This follows from the results shown in chapter 5.

It follows for the last block that

$$\lim_{\ell\to\infty}\lim_{n\to\infty} \int_0^T dt \int \bar{r}_{n/\ell-1,\ell} f^n_t \, d\mu^{c,n}_{\bar{\tau}(t),\beta} = 0.$$

To conclude we have to show that all blocks will have, in the limit, the same density of r_i, i.e. that

$$\lim_{\ell\to\infty}\lim_{n\to\infty} \frac{\ell}{n} \sum_{j=0}^{n/\ell-2} \int_0^T dt \int \left|\bar{r}_{n/\ell-1,\ell} - \bar{r}_{j,\ell}\right| f^n_t \, d\mu^{c,n}_{\bar{\tau}(t),\beta} = 0. \tag{3.2.6}$$

This last limit also follows from (3.2.4), by the so called two-block lemma. It is enough to prove that , for any j, we have

$$\lim_{\ell\to\infty}\lim_{n\to\infty} \int_0^T dt \int \frac{\left(\partial_{r_{j\ell}} f^n_t - \partial_{r_n} f^n_t\right)^2}{f^n_t} \, d\mu^{c,n}_{\bar{\tau}(t),\beta} = 0.$$

This can be proved by a telescoping argument, since

$$\left(\partial_{r_{j\ell}} f_t^n - \partial_{r_n} f_t^n\right)^2 \leq n \sum_{i=1}^{n-1} \left(\partial_{r_{i+1}} f_t^n - \partial_{r_i} f_t^n\right)^2 = n \sum_{i=1}^{n-1} \left(\partial_{q_i} f_t^n\right)^2$$

and using (3.2.4) the result follows. □

3.3 Work and Microscopic Heat

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

$$\mathcal{L}_n(t) = \frac{q_n(t)}{n} = \frac{1}{n} \sum_{i=1}^{n} r_i(t). \tag{3.3.1}$$

The time evolution in the scale considered is given by

$$\mathcal{L}_n(t) - \mathcal{L}_n(0) = \int_0^t n^{1+\alpha} p_n(s)\, ds. \tag{3.3.2}$$

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

$$\mathcal{L}_n(0) \underset{n\to\infty}{\longrightarrow} r_0, \tag{3.3.3}$$

in probability, and the quasi static limit proven above says that

$$\mathcal{L}_n(t) \underset{n\to\infty}{\longrightarrow} \bar{r}(t). \tag{3.3.4}$$

The internal energy is defined as

$$U_n := \frac{1}{n} \sum_{i=1}^{n} \left(\frac{p_i^2}{2} + V(r_i) \right) \tag{3.3.5}$$

and it evolves as:

$$U_n(t) - U_n(0) = \mathcal{W}_n(t) + Q_n(t) \tag{3.3.6}$$

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

$$Q_n(t) = \gamma\, n^{1+\alpha} \sum_{j=1}^{n} \int_0^t ds \left(p_j^2(s) - \beta^{-1}\right) + n^{\alpha/2} \sum_{j=1}^{n} \sqrt{2\gamma\beta^{-1}} \int_0^t p_j(s) dw_i(s). \tag{3.3.7}$$

is the total flux of energy between the system and the heat bath (divided by n). As a consequence of (3.1.13) we have that

$$\lim_{n\to\infty} \mathcal{W}_n(t) = \int_0^t \bar{\tau}(s) d\bar{r}(s) := \mathcal{W}(t). \tag{3.3.8}$$

While for the energy difference we expect that

$$\lim_{n\to\infty} \left(U_n(t) - U_n(0)\right) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) \tag{3.3.9}$$

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

$$u(\tau, \beta) = -\partial_\beta \tilde{\mathcal{G}}(\tau, \beta)$$

By (3.3.6) (3.3.8) and (3.3.9) we have

$$Q_n(t) \underset{n\to\infty}{\longrightarrow} Q(t) \tag{3.3.10}$$

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

$$Q(t) = u(\bar{\tau}(t), \beta) - u(\bar{\tau}(0), \beta) - \mathcal{W}(t). \tag{3.3.11}$$

which is the first principle of thermodynamics for quasistatic transformations.

Free energy and Clausius identity

Taking the time derivatiove of the free energy $\mathcal{F}(\bar{r}(t), \beta)$

$$\frac{d}{dt}\mathcal{F}(\bar{r}(t), \beta) = \tilde{\tau}(t)\bar{r}'(t),$$

it means

$$\mathcal{F}(\bar{r}(t), \beta) - \mathcal{F}(\bar{r}(0), \beta) = \int_0^t \bar{\tau}(s) d\bar{r}(s) = \mathcal{W}(t) \tag{3.3.12}$$

i.e. Clausius equality for the free energy.

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

$$\beta^{-1}\left(S(\bar{r}(t), u(t)) - S(\bar{r}(0), u(0))\right) = Q(t) \tag{3.3.13}$$

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

3.4 Comments on the literature

[13], [3], [11],

Chapter 4

Quasi-Static Adiabatic Transformations

From the mathematica point of view, the deduction of the isothermal trasformation is quite satrisfactory. This is due to the fact that, because of the presence of the heat bath in the microscopic dynamics, this is intrinsicaly stochastic and consequently it has very good ergodic properties.

The situation is much more difficult for the adiabatic dynamics. In principle the system is isolated except for the presence of the exterior tension, so the dynamics is deterministic. Little is know about convergence to equilibrium for deterministic dynamics, especially when also the dimension of the system is infinite. The basic problem is the possible existence of other conserved quantities beside the energy, volume and eventually momentum that may persists even when the dimension of the system goes to infinity. Some help can be obtained considering stochastic perturbation ot the dynamics, such that volume and energy (and even momentum sometimes) remain conserved but all other integral of the motion are destroyed by the noise [14] [12] [5] .

4.1 The adiabatic dynamics

$$\begin{aligned} dr_i &= n^{1+\alpha}(p_i - p_{i-1})\, dt \\ dp_i &= n^{1+\alpha}(V'(r_{i+1}) - V'(r_i))\, dt, \qquad i = 1, \dots, n-1, \\ dp_n &= n^{1+\alpha}(\bar{\tau}(t) - V'(r_n))\, dt \end{aligned} \tag{4.1.1}$$

p_0 is set identically to 0, and $\alpha > 0$. The case $\alpha = 0$ will be the natural hyperbolic space-time scaling where Euler equations would describe the macroscopic evolution

[5]. Notice that the external force $\bar{\tau}(t)$ changes at the macroscopic time scale. Setting $\alpha > 0$ will only ensure to be in a time scale where mechanical equilibrium is reached, but in order to obtain also thermal equilibrium we should set larger $\alpha > 1$[1]

4.2 The quasi-static limit

We would like to obtain that the distribution at time $t > 0$ is close to a Gibbs canonical measure $\mu^{c,n}_{\bar{\tau}(t),\beta(t)}$, but we have first to determine what would be the temperature $\beta(t)^{-1}$ at time t.

We start at $t = 0$ with the equilibrium $\mu^{c,n}_{\bar{\tau}(0),\beta(0)}$. Correspondingly there is an average energy $e(0)$ give by

$$e(0) = u(\beta(0), \tau(0)) = -\partial_\beta \mathcal{G}(\beta(0), \tau(0))$$

The macroscopic work done by the force $\bar{\tau}(\cdot)$ up to time t is given by

$$W(t) = \int_0^t \bar{\tau}(s) dr(s),$$

i.e.

$$W'(t) = \bar{\tau}(s) r'(s)$$

where $r(t)$ is the average stretch at time t given by

$$r(t) = \mathbf{r}(\beta(t), \bar{\tau}(t)) = \beta(t)^{-1} (\partial_\tau \mathcal{G})(\beta(t), \bar{\tau}(t))$$

Then the energy at time t, by the first law, is given by

$$e(t) = e(0) + W(t)$$

that gives the temperature at time t as

$$\beta(t) = (\partial_e S)(e(t), r(t)).$$

This transformation keeps entropy constant:

$$S(e(t), r(t)) - S(e(0), r(0)) = \int_0^t \left(\beta(s) e'(s) - \beta(s)\bar{\tau}(s) r'(s)\right) ds = 0.$$

---

[1] Probably less will be enough in this one dimensional system as thermal energy is expected to superdiffuse.

Let us denote by $f_t^n(r_1, p_1, \dots, r_n, p_n)$ the probability density of the configurations at time t with respect to $\mu^{c,n}_{\bar\tau(t),\beta(t)}$, i.e. the solution of

$$\partial_t \left(f_t^n g^n_{\bar\tau(t),\beta(t)} \right) = -n^{1+\alpha} \left(\mathcal{A}_n^{\bar\tau(t)} f_t^n \right) g^n_{\bar\tau(t),\beta(t)}, \qquad f_0^n = 1, \tag{4.2.1}$$

where

$$\begin{aligned} A_n^\tau \;&=\; \sum_{i=1}^n (p_i - p_{i-1}) \frac{\partial}{\partial r_i} + \sum_{i=1}^{n-1} \left(V'(r_{i+1}) - V'(r_i) \right) \frac{\partial}{\partial p_i} \\ &\quad + \left(\tau - V'(r_n) \right) \frac{\partial}{\partial p_n}, \end{aligned} \tag{4.2.2}$$

As in the isothermal quasi static limit, what we would like to have for the relative entropy $H_n(t)$ is that

$$\lim_{n\to\infty} \frac{H_n(t)}{n} = 0. \tag{4.2.3}$$

Let us see what is the difficulty here. As in the isothermal case, let's take the time derivative:

$$\frac{d}{dt} H_n(t) = - \int f_t^n \partial_t g^n_{\beta(t),\bar\tau(t)} \prod_{j=1}^n dr_j dp_j. \tag{4.2.4}$$

$$\partial_t g^n_{\beta(t),\bar\tau(t)} = \left[-\beta'(t) \sum_{j=1}^n \left(\mathcal{E}_j - e(t) \right) + \left(\beta(t)\bar\tau(t) \right)' \sum_{j=1}^n \left(r_j - \mathfrak{r}(\bar\tau(t)) \right) \right] g^n_{\bar\tau(t)}.$$

That gives

$$\frac{d}{dt} H_n(t) = \int \sum_{j=1}^n \left[-\beta'(t) \left(\mathcal{E}_j - e(t) \right) + \left(\beta(t)\bar\tau(t) \right)' \left(r_j - r(t) \right) \right] f_t^n d\mu^{c,n}_{\bar\tau(t),\beta(t)} \tag{4.2.5}$$

Then all one has to prove is that this last quantity divided by n goes to 0, i.e. that

$$\begin{aligned} \lim_{n\to\infty} \int_0^T dt \left[\int \frac{1}{n} \sum_{j=1}^n \mathcal{E}_j f_t^n d\mu^{c,n}_{\bar\tau(t),\beta(t)} - e(t) \right] = 0 \\ \lim_{n\to\infty} \int_0^T dt \left[\frac{1}{n} \int q_n f_t^n d\mu^{c,n}_{\bar\tau(t),\beta(t)} - r(t) \right] = 0 \end{aligned} \tag{4.2.6}$$

So we have that (4.2.6) are necessary and sufficient conditions for the validity of the adiabatic quasi static limit.

4.3 A stochastic dynamics

The limits (4.2.6) are difficult to be establish for a deterministic dynamics, and this stays an open problem. To establish the limit (4.2.6) implies to have enough ergodic properties of the dynamics such that at the boundary the volum stretch and the energy get close to the desired ones, and because the quast-static time scale, this diffuse to the entire system.

Perturbing the dynamics with stochastic terms that conserves energy and volume will help in this task. One easy way is to add random exchanges between nearest neighbors of momentum and interparticle distance, i.e. exchange

$$p_j \leftrightarrow p_{j+1} \qquad r_j \leftrightarrow r_{j+1} \tag{4.3.1}$$

independently with rates $n^{1+\alpha}$, $\alpha > 1$. This means to consider the dynamics generated by

$$\mathcal{L}_n = n^{1+\alpha} A_n^{\bar\tau(t)} + \gamma_p n^{1+\alpha} S_n^p + \gamma_r n^{1+\alpha} S_n^r \tag{4.3.2}$$

with

$$\begin{aligned} S_n^p F(\mathbf{r},\mathbf{p}) &= \sum_{j=1}^{n-1} \big(F(\mathbf{r},\mathbf{p}^{j,j+1}) - F(\mathbf{r},\mathbf{p})\big) \\ S_n^r F(\mathbf{r},\mathbf{p}) &= \sum_{j=1}^{n-1} \big(F(\mathbf{r}^{j,j+1},\mathbf{p}) - F(\mathbf{r},\mathbf{p})\big) \end{aligned} \tag{4.3.3}$$

Observe that this stochastic perturbations of the dynamics conserve the total energy, total volume and the total momentum.

For this stochastic dynamics we can prove:

Theorem 4.3.1.

$$\lim_{n\to\infty} \frac{H_n(t)}{n} = 0. \tag{4.3.4}$$

Proof. The stochastic terms contribute with non-negative terms to the derivatiove of the relative entropy:

$$\begin{aligned} \frac{d}{dt} H_n(t) &= \int \sum_{j=1}^{n} \left[-\beta'(t)\left(\mathcal{E}_j - e(t)\right) + \left(\beta(t)\bar\tau(t)\right)'\left(r_j - r(t)\right)\right] f_t^n \, d\mu^{c,n}_{\bar\tau(t),\beta(t)} \\ -\gamma^p n^{1+\alpha} &\int \sum_{j=1}^{n-1} \big(f_t^n(\mathbf{r},\mathbf{p}^{j,j+1}) - f_t^n(\mathbf{r},\mathbf{p})\big)\big(\log f_t^n(\mathbf{r},\mathbf{p}^{j,j+1}) - \log f_t^n(\mathbf{r},\mathbf{p})\big)\, d\mu^{c,n}_{\bar\tau(t),\beta(t)} \\ -\gamma^r n^{1+\alpha} &\int \sum_{j=1}^{n-1} \big(f_t^n(\mathbf{r}^{j,j+1},\mathbf{p}) - f_t^n(\mathbf{r},\mathbf{p})\big)\big(\log f_t^n(\mathbf{r}^{j,j+1},\mathbf{p}) - \log f_t^n(\mathbf{r},\mathbf{p})\big)\, d\mu^{c,n}_{\bar\tau(t),\beta(t)} \end{aligned} \tag{4.3.5}$$

By the inequality $a\log(b/a) \le 2\sqrt{a}(\sqrt{b} - \sqrt{a})$ we have

$$\begin{aligned}\frac{d}{dt}H_n(t) = &\int \sum_{j=1}^{n} \left[-\beta'(t)\left(\mathcal{E}_j - e(t)\right) + \left(\beta(t)\bar\tau(t)\right)'\left(r_j - r(t)\right)\right] f_t^n \, d\mu^{c,n}_{\bar\tau(t),\beta(t)} \\ &-\gamma^p n^{1+\alpha} \int \sum_{j=1}^{n-1} \left(\sqrt{f_t^n(\mathbf{r},\mathbf{p}^{j,j+1})} - \sqrt{f_t^n(\mathbf{r},\mathbf{p})}\right)^2 d\mu^{c,n}_{\bar\tau(t),\beta(t)} \\ &-\gamma^r n^{1+\alpha} \int \sum_{j=1}^{n-1} \left(\sqrt{f_t^n(\mathbf{r}^{j,j+1},\mathbf{p})} - \sqrt{f_t^n(\mathbf{r},\mathbf{p})}\right)^2 d\mu^{c,n}_{\bar\tau(t),\beta(t)}\end{aligned}$$

From this, by intyegrating in time and using entropy inequality and energy bounds one obtains

$$H_n(t) \le cn,$$

and

$$\begin{aligned}\gamma^p \int \sum_{j=1}^{n-1} \left(\sqrt{f_t^n(\mathbf{r},\mathbf{p}^{j,j+1})} - \sqrt{f_t^n(\mathbf{r},\mathbf{p})}\right)^2 d\mu^{c,n}_{\bar\tau(t),\beta(t)} \le cn^{-\alpha} \\ \gamma^r \int \sum_{j=1}^{n-1} \left(\sqrt{f_t^n(\mathbf{r}^{j,j+1},\mathbf{p})} - \sqrt{f_t^n(\mathbf{r},\mathbf{p})}\right)^2 d\mu^{c,n}_{\bar\tau(t),\beta(t)} \le cn^{-\alpha}\end{aligned} \tag{4.3.6}$$

In the limit the distribution will get the right excheangeability properties to propagate the ergodicity at the boundary to the system inside. *Details will follow soon* □

4.4 Comments on the literature

[10],

Chapter 5

Dynamics

In this chapter we study the dynamics of the infinite chain and we set the problem of its ergodicity. We need first to give a proper definition of ergodicity for an infinite dynamics. We need some stochastic perturbation in order to prove something about this ergodicity. We introduce then some stochastic perturbation acting only on the velocities such that will conserve the total energy and momentum of the chain.

5.1 Dynamics of the infinite system

In order to avoid technical difficulties we assume the potential V satisfies

$$V'(r)^2 \le CV(r), \qquad V''(r) \le C \tag{5.1.1}$$

Basically we require that V grows to infinity quadratically.

We consider now the system in the infinite lattice $\mathbb{Z}$. As before, $r_j = q_j - q_{j-1}$ is the interparticle distance. Let us denote $\Omega = (\mathbb{R}^2)^{\mathbb{Z}}$ the configuration space and $\omega = (p_i, r_i)_{i \in \mathbb{Z}} \in \Omega$ the generic configuration. We introduce the space $C_0^k(\Omega)$ composed of local functions which are k differentiable with continuous bounded derivatives and $\mathcal{D}(\Omega) = \cap_{k \ge 0} C_0^k(\Omega)$.

The hamiltonian dynamics is given by the solution of the infinite system of differential equations

$$\begin{aligned} \dot{r}_j(t) &= p_j(t) - p_{j-1}(t) \\ \dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j \in \mathbb{Z}. \end{aligned} \tag{5.1.2}$$

and the formal *generator* of the dynamics is the Liouville operator

$$\mathcal{A} = \sum_{j \in \mathbb{Z}} \left\{ (p_j - p_{j-1})\, \partial_{r_j} + (V'(r_{j+1}) - V'(r_j))\, \partial_{p_j} \right\} \tag{5.1.3}$$

with domain $\mathcal{D}(\Omega)$.

The existence of the solution for (5.1.2) can be proven for a wide class of initial conditions, in particular for a set of configurations that has measure one for any Gibbs grand-canonical distribution

$$d\mu^{gc}_{\tau,\bar{p},\beta} = \prod_{j\in\mathbb{Z}} \frac{e^{-\beta(\mathcal{E}_j - \bar{p}p_j - \tau r_j)}}{\mathcal{Z}(\beta\tau, \beta\bar{p}, \beta)} dr_j dp_j \ . \tag{5.1.4}$$

for all parameters $\tau, \bar{p}, \beta > 0$. We will prove this existence by an iteration scheme. Notice that the momentum is formally conserved, which follows from the translation invariance of the dynamics. This is why we have the third parameter $\bar{p}$ in the stationary measures.

A set of initial conditions can be defined in the following way. For $a > 0$, we denote

$$\Omega_a = \left\{ \omega = (r_j, p_j)_{j\in\mathbb{Z}} \in (\mathbb{R}^2)^{\mathbb{Z}} \ : \ \|\omega\|_a^2 = \sum_{j\in\mathbb{Z}} (p_j^2 + r_j^2) e^{-a|j|} < \infty \right\}$$

the Hilbert space equipped with the norm $\|\cdot\|_a$. It is easy to check that any probability measure ν such that $\int (r_j^2 + p_j^2) d\nu \le Ce^{bj}$ with $b < a$ gives measure one to Ω_a. In particular any Gibbs measure $\mu^{gc}_{\tau,\bar{p},\beta}$ satisfies this condition since

$$\int r^2 e^{-\beta(V(r) - \tau r)} dr \le C\left[Z(\tau\beta + 1, \beta) + Z(\tau\beta - 1, \beta)\right]$$

We also introduce the Banach space $\mathcal{H}_a$ composed of all continuous Ω_a-valued functions ω on the time interval $[0, T]$ with norm

$$N(\omega) = \sup_{t\in[0,T]} \|\omega(t)\|_a$$

The two next lemmas are proved in a more general context in section 5.3.

Lemma 5.1.1. *For any $\sigma \in \Omega_a$, there exists a unique stochastic process $\omega(\cdot, \sigma) = (r_i(\cdot), p_i(\cdot))_{i\in\mathbb{Z}}$ belonging to $\mathcal{H}_a$ and satisfying (5.3.5) with initial condition $\omega(0, \sigma) = \sigma$. The application $\sigma \in \Omega_a \to \omega(\cdot, \sigma) \in \mathcal{H}_a$ is continuously differentiable.*

For any $\omega \in \Omega_a$, the quantity $\left[\sum_j e^{-a|j|}\mathcal{E}_j(\omega)\right]$ is finite (thanks to (5.1.1)). Starting from ω, (5.1.1) gives

$$\frac{d}{dt}\left(\sum_{j\in\mathbb{Z}} e^{-a|j|}\mathcal{E}_j(\omega(t))\right) \le C \sum_{j\in\mathbb{Z}} e^{-a|j|}\mathcal{E}_j(\omega(t)) \tag{5.1.5}$$

and then the following a priori bound

$$\left[\sum_{j\in\mathbb{Z}} e^{-a|j|}\mathcal{E}_j(\omega(t))\right] \le C_0 e^{c_1 t}\left[\sum_{j\in\mathbb{Z}} e^{-a|j|}\mathcal{E}_j(\omega)\right] \tag{5.1.6}$$

We define a semigroup $(P_t)_{t\geq 0}$ on the space $B(\Omega_a)$ of bounded measurable functions on Ω_a by:

$$\forall f \in B(\Omega_a), \quad \forall \sigma \in \Omega_a, \quad (P_t f)(\sigma) = f(\omega(t,\sigma))$$

where $\omega(t,\sigma) = \{r_j(t), p_j(t);\ j \in \mathbb{Z}\}$ is the solution of (5.1.2) starting from σ.

We have the following lemma

Lemma 5.1.2. *Stationary states μ satisfying the moment condition*

$$\sup_{j\in\mathbb{Z}} \int \mathcal{E}_j d\mu < +\infty \tag{5.1.7}$$

are characterized by the stationary Kolmogorov equation:

$$\int \mathcal{A}\phi(\omega)d\mu(\omega) = 0 \textit{ for } \ \phi \in \mathcal{D}(\Omega)$$

The moment condition (5.3.3) is here to ensure that the support of μ is included in $\cap_{a>0}\Omega_a$.

5.2 Ergodicity

Ergodicity is one of the main open problem for Hamiltonian systems, in fact we think there is not a general agreement on what it means for an infinite system.

For us *ergodicity* will mean a characterization of the stationary translation invariant probability measure, in a class of *locally regular* measure, as convex combination of Gibbs measures.

Definition 5.2.1. *We say that the dynamics defined by (5.1.2) is ergodic if any probability measure ν on the configuration space that*

1. *has finite density entropy :* $\exists C > 0, \forall \Lambda \Subset \mathbb{Z}, \quad H_\Lambda(\nu|\mu^{gc}_{0,0,1}) \le C|\Lambda|$
2. *is translation invariant,*

3. is stationary, i.e. for any function $F(r,p) \in \mathcal{D}(\Omega)$

$$\int \mathcal{A}F \; d\nu = 0 \tag{5.2.1}$$

is a convex combination of Gibbs measures $\mu^{gc}_{\tau,\bar{p},\beta}$.

Remark 5.2.2. *In the first assumption* $\mu^{gc}_{0,0,1}$ *does not play any role and can be replaced by any Gibbs measure* $\mu^{gc}_{\tau,\bar{p},\beta}$.

It is clear that this property is not always true. The easier example is the harmonic case, i.e. V quadratic. We are tempted to conjecture that for generic non-linear dynamics the system is ergodic. But for Toda lattice interaction $V(r) = ae^r - r - b$, the dynamics is completely integrable in its finite dimensional version (like the harmonic case) and constitute another conterexample. So it is not clear on which class of anharmonic V the ergodic property can be conjectured.

The idea is that the nonlinearity should mess up sufficiently the distribution of the velocity.

Theorem 5.2.3. *Let* ν *satisfy the three conditions of definition 5.2.1, and furthermore the distribution of the velocities conditioned to the position* $\nu(dp|r)$ *is excheangeable. Then* ν *is a convex combination of Gibbs measures* $\mu^{gc}_{\tau,\bar{p},\beta}$.

Let $\mathcal{F}_{inv}$ be the σ-field of the sets of Ω invariant for translations.

Lemma 5.2.4. *If* ν *is a translation invariant probability measure on* Ω *such that* $\nu(dp|r)$ *is exchangeable then conditionally to* $\mathcal{F}_{inv}$ *the p's and the r's.*

Proof:

Let $\mathcal{F}_k$ be the σ-field generated by $\{\omega_x, x \in \{-k,\dots,k\}\}$. A measurable transformation $T : \Omega \to \Omega$ is called local if $T(\omega)$ is $\mathcal{F}_k$-measurable for some $k \geq 1$. For example the map $T_{x,y} : (p,r) \to (p^{x,y}, r)$, where $p^{x,y}$ is the configuration of velocities obtained by the exchange of p_x and p_y, is a local transformation. Any bounded function θ is the limit of $\theta_k = \nu(\theta|\mathcal{F}_k)$ as $k \to \infty$ a.s. and in mean square. Let θ be a bounded $\mathcal{F}_{inv}$-measurable function. Then $\theta = \nu(\theta|\mathcal{F}_{inv}) = \lim_{k\to\infty} \nu(\theta_k|\mathcal{F}_{inv})$ a.s. and in mean square and using the ergodic theorem we have

$$\theta = \lim_{k\to\infty} \lim_{N\to\infty} \frac{1}{2N+1} \sum_{j=-N}^{N} \tau_j \theta_k \tag{5.2.2}$$

Since θ_k is a local function for any k this shows that any $\mathcal{F}_{inv}$-measurable function is in fact invariant w.r.t. any local transformation T.

Let $\phi(r)$ and $\psi(p)$ be two bounded local functions depending respectively only on the velocities and on the positions. Let θ be a bounded $\mathcal{F}_{inv}$-measurable function. Consider two integers k and j. Since ψ is local there exists a local transformation T_k obtained as the composition of exchange transformations $T_{x,y}$ such that $T_k\psi(p) = \tau_k\phi(p)$. Let $\chi_k(r) = \nu(\psi(\tau_k p)\theta(p,r)|r)$ and observe that $\chi_0(r) = \nu\left(\psi(T_k p)\theta(T_k p, r)|r\right) = \nu\left(\psi(\tau_k p)\theta(p,r)|r\right) = \chi_k(r)$ because $\nu(dp|r)$ is T_k-invariant and θ is T_k-invariant.

Observe also that $\chi_k(\tau_j r) = \chi_{j+k}(r)$. Then we have

$$\begin{aligned}
\int \phi(r)\psi(p)\;\theta(p,r)\;d\nu &= \int \nu(\phi\psi|\mathcal{F}_{inv})\;\theta\;d\nu \\
&= \int \phi(r)\chi_0(r)\;d\nu = \int \phi(r)\chi_k(r)\;d\nu \\
&= \int \phi(\tau_j r)\chi_k(\tau_j r)\;d\nu = \int \phi(\tau_j r)\psi(\tau_{k+j}p)\theta(p,r)\;d\nu \\
&= \int \phi(r)\psi(\tau_k p)\theta(p,r)\;d\nu
\end{aligned}$$

We now sum over $k = -N \dots N$ and divide by $(2N+1)$. Taking the limit $N \to \infty$ ergodic theorem implies

$$\int \nu(\phi\psi|\mathcal{F}_{inv})\theta\;d\nu = \int \nu(\phi|\mathcal{F}_{inv})\mu(\psi|\mathcal{F}_{inv})\theta\;d\nu \tag{5.2.3}$$

and the claim is proved.

$\square$

Because ν has finite entropy density the entropy inequality (proposition **??**) gives the following bound on the energy density

$$\exists C > 0, \forall j \in \mathbb{Z}, \qquad \int \mathcal{E}_j d\nu \le C \tag{5.2.4}$$

Then the ergodic theorem allows us to define ν a.s. the following quantities

$$\begin{aligned}
z_0 &= \lim_{\ell\to\infty} z_0^\ell = \lim_{\ell\to\infty} \frac{1}{\ell}\sum_{j=1}^{\ell} r_j = \nu(r_j|\mathcal{F}_{inv}) \\
z_1 &= \lim_{\ell\to\infty} z_1^\ell = \lim_{\ell\to\infty} \frac{1}{\ell}\sum_{j=1}^{\ell} p_j = \nu(p_j|\mathcal{F}_{inv}) \\
z_2 &= \lim_{\ell\to\infty} z_2^\ell = \lim_{\ell\to\infty} \frac{1}{\ell}\sum_{j=1}^{\ell} p_j^2 = \nu(p_j^2|\mathcal{F}_{inv})
\end{aligned}$$

and we denote by $\mathbf{z}(r,p) = (z_0, z_1, z_2)$ the corresponding random vector (with values on $\mathbb{R} \times \mathbb{R} \times \mathbb{R}_+$). Denote $\hat{\beta}$ the $\mathcal{F}_{inv}$-measurable function defined by

$$\hat{\beta}^{-1} = \nu(p_j(p_j - z_1)|\mathcal{F}_{inv}) = z_2 - z_1^2 \tag{5.2.5}$$

and observe that

$$\hat{\beta}^{-1}\delta_{i,j} = \nu(p_i(p_j - z_1)|\mathcal{F}_{inv}) \tag{5.2.6}$$

Let us first show that the degenerate situation of null temperature: $\hat{\beta}^{-1} = 0$ is impossible. We have

Lemma 5.2.5. *Let ν a translation invariant measure with finite entropy density. Then ν a.s. we have $z^2 - z_1^2 > 0$.*

Proof :

Let $A_{\ell,\varepsilon}$ be the event

$$A_{\ell,\varepsilon} = \left\{ \left| \frac{1}{\ell}\sum_{j=1}^{\ell} p_j^2 - \left(\frac{1}{\ell}\sum_{j=1}^{\ell} p_j\right)^2 \right| \leq \varepsilon \right\} \in \mathcal{F}_{\Lambda_\ell}$$

By the entropy inequality we have

$$\nu(A_{\ell,\varepsilon}) \leq \frac{\log 2 + H_{\Lambda_\ell}(\nu|\mu)}{\log(1 + \mu(A_{\ell,\varepsilon})^{-1})} \leq \frac{C_0 \ell}{\log(1 + \mu(A_{\ell,\varepsilon})^{-1})} \tag{5.2.7}$$

for some constant C_0 independent of ℓ. Moreover it is well known that

$$\frac{1}{\ell}\sum_{j=1}^{\ell} p_j^2 - \left(\frac{1}{\ell}\sum_{j=1}^{\ell} p_j\right)^2 = \frac{1}{\ell}\sum_{j=1}^{\ell}\left(p_j - \left(\frac{1}{\ell}\sum_{j=1}^{\ell} p_j^2\right)\right)^2$$

has the same law as $\ell^{-1}\sum_{j=1}^{\ell-1} p_j^2$. By Cramer theorem **??** we have

$$\mu(A_{\ell,\varepsilon}) = \mu\left(\ell^{-1}\sum_{j=1}^{\ell-1} p_j^2 \leq \varepsilon\right) \sim e^{-\ell \inf_{x \leq \varepsilon} I(x)}$$

where I is the large deviations rate function associated to $(p_j^2)_{j=1,\ldots,\ell}$. A simple computation shows that $\inf_{x\leq\varepsilon} I(x) = I(\varepsilon)$ goes to $+\infty$ as $\varepsilon \to 0$. Letting first ℓ going to $+\infty$ and then $\varepsilon \to 0$ we get

$$\nu(z_2 - z_1^2 = 0) = 0$$

□

Lemma 5.2.6. *For any function $F \in \mathcal{D}(\Omega)$ and any bounded $\mathcal{F}_{inv}$-measurable function h we have*

$$\int h(r,p)\, \mathcal{A}F(r,p)\, d\nu(r,p) = 0 \ .$$

Proof: Clearly it is sufficient to prove the lemma for h in the form $h(\omega) = \pi(p)\rho(r)$ where π (resp. ρ) is a bounded $\mathcal{F}_{inv}$-measurable functions of the p's (resp. of the r's). We use the following approximations similar to (5.2.2) for π and ρ:

$$\pi(p) = \lim_{k\to\infty} \pi_k^{(N)}(p) = \lim_{k\to\infty}\lim_{N\to\infty} \frac{1}{2N+1}\sum_{j=-N}^{N} \tau_j \pi_k(p)$$

$$\rho(r) = \lim_{k\to\infty} \rho_k^{(N)}(r) = \lim_{k\to\infty}\lim_{N\to\infty} \frac{1}{2N+1}\sum_{j=-N}^{N} \tau_j \rho_k(r)$$

where π_k (resp. ρ_k) is a smooth local function measurable w.r.t. the σ-filed $\mathcal{F}_k^p$ (resp. $\mathcal{F}_k^r$) generated by (p_x), $x \in \{-k,\dots,k\}$ (resp. (r_x), $x \in \{-k,\dots,k\}$). In fact the local function π_k (resp. ρ_k) is a smooth approximation of $\nu(\pi|\mathcal{F}_k^p)$ (resp. $\nu(\rho|\mathcal{F}_k^r)$).

Since π_k, ρ_ℓ and F are smooth functions, (5.2.1) implies

$$\int \pi_k^{(N)}\rho_\ell^{(M)} \mathcal{A}F\, d\nu \;\; = \;\; -\int F\left[\mathcal{A}\pi_k^{(N)}\,\rho_\ell^{(M)} + \pi_k^{(N)}\mathcal{A}\rho_\ell^{(M)}\right] d\nu$$

Observe that

$$\mathcal{A}(\pi_k^{(N)}) = \frac{1}{2N+1}\sum_{j=-N}^{N} \tau_j \left[\sum_{i\in\mathbb{Z}} (V'(r_{i+1}) - V'(r_i))\partial_{p_i}\pi_k\right]$$

converges ν a.s. as N goes to infinity to

$$\nu\left(\sum_{i\in\mathbb{Z}}(V'(r_{i+1}) - V'(r_i))\partial_{p_i}\pi_k|\mathcal{F}_{inv}\right) = \sum_{i\in\mathbb{Z}} \nu\left((V'(r_{i+1}) - V'(r_i))|\mathcal{F}_{inv}\right)\nu\left(\partial_{p_i}\pi_k|\mathcal{F}_{inv}\right) = 0$$

by lemma 5.2.4. Hence we have

$$\lim_{k\to\infty}\lim_{N\to\infty}\int \pi_k^{(N)}\rho_\ell^{(M)}\mathcal{A}F\, d\nu = -\int F\pi\mathcal{A}\rho_\ell^{(M)} d\nu$$

and similarly we have that $\mathcal{A}\rho_\ell^{(M)}$ converges ν a.s. as M goes to infinity to 0. It follows that

$$\int \pi\rho\mathcal{A}F d\nu = \lim_{\ell\to\infty}\lim_{M\to\infty}\lim_{k\to\infty}\lim_{N\to\infty}\int \pi_k^{(N)}\rho_\ell^{(M)}\mathcal{A}F\, d\nu = 0$$

which completes the proof. □

Proof of Theorem 5.2.3.

It follows from lemma 5.2.6 that for every $F(r,p) \in \mathcal{D}(\Omega)$

$$\int \mathcal{A}F(r,p)\, d\nu(r,p|\mathcal{F}_{inv}) = 0 \ . \tag{5.2.8}$$

Choosing in (5.2.8) the function

$$F = (p_j - z_1)\phi(r)$$

with $\phi(r) \in \mathcal{D}(\mathbb{R}^{\mathbb{Z}})$ that we specify later, we obtain by lemma 5.2.4

$$\begin{aligned} 0 &= \int \left\{ \sum_i (p_j - z_1) p_i \left(\partial_{r_i}\phi - \partial_{r_{i+1}}\phi\right) + \left(V'(r_{j+1}) - V'(r_j)\right)\phi(r) \right\} \, d\nu(r,p|\mathcal{F}_{inv}) \\ &= \sum_i \left(\int (p_j - z_1) p_i \nu(dp|\mathcal{F}_{inv}) \right) \left(\int \left(\partial_{r_i}\phi - \partial_{r_{i+1}}\phi\right) d\nu(r|\mathcal{F}_{inv}) \right) \\ &\quad + \int \left(V'(r_{j+1}) - V'(r_j)\right)\phi(r)\, d\nu(r|\mathcal{F}_{inv}) \\ &= \int \left\{ \hat\beta^{-1} \left(\partial_{r_j}\phi - \partial_{r_{j+1}}\phi\right) + \left(V'(r_{j+1}) - V'(r_j)\right)\phi(r) \right\} \, d\nu(r|\mathcal{F}_{inv}) \ . \end{aligned} \tag{5.2.9}$$

Define

$$\psi_\ell(r) = e^{\sum_{i=1}^{\ell} (\hat\beta V(r_i) - \hat\lambda r_i)}$$

where $\hat\lambda = \lambda(z_0, \hat\beta)$. Notice that $\hat\lambda$ and $\hat\beta$ are just function of $\mathbf{z}$, so we can treat them as constant under $\nu(dr|\mathcal{F}_{inv})$. Choosing

$$\phi(r) = \chi(r)\psi_\ell(r),$$

with $\chi(r)$ a local smooth function, we get for any $j = 1, \ldots, \ell - 1$:

$$\int \hat\beta^{-1} \left(\partial_{r_j}\chi - \partial_{r_{j+1}}\chi\right) \psi_l(r)\, d\nu(r|\mathcal{F}_{inv}) = 0 \ .$$

We choose now

$$\chi(r) = \chi_b(r) g\left(\sum_{i=1}^{\ell} r_i \right) \chi_0(r_1, \ldots, r_{\ell-1}),$$

where χ_b is a local function not depending on $r_1, \dots, r_\ell$, and g is a smooth function on $\mathbb{R}$. Since

$$\partial_{r_j}\chi(r) - \partial_{r_{j+1}}\chi(r) = \chi_b(r) g\left(\sum_{i=1}^{\ell} r_i\right)\left(\partial_{r_j}\chi_0(r) - \partial_{r_{j+1}}\chi_0(r)\right)$$

if $j = 1, \dots, \ell - 1$, we can further condition on $\sum_{k=1}^{\ell} r_k = \ell u$ and on the exterior configuration $\{r_i, i \neq 1, \dots, \ell\}$, and obtain, for all $j = 1, \dots, \ell - 1$,

$$\int \left(\partial_{r_j}\chi_0(r) - \partial_{r_{j+1}}\chi_0(r)\right)\psi_l(r) \\ \nu\left(dr_1, \dots, dr_\ell \Big| \sum_{k=1}^{\ell} r_k = \ell u, r_i,\ i \neq 1, \dots, \ell, \mathcal{F}_{inv}\right) = 0 \tag{5.2.10}$$

This is enough to characterize the measure

$$\psi_l(r)\nu\left(dr_1, \dots, dr_\ell \Big| \sum_{k=1}^{\ell} r_k = \ell u, r_i,\ i \neq 1, \dots, \ell, \mathcal{F}_{inv}\right) = \\ = e^{-\ell\hat{\lambda}r}\prod_{i=1}^{\ell} e^{\hat{\beta}V(r_i)}\nu\left(dr_1, \dots, dr_\ell \Big| \sum_{k=1}^{\ell} r_k = \ell u, r_i,\ i \neq 1, \dots, \ell, \mathcal{F}_{inv}\right)$$

as the Lebesgue measure on the hyperplane $\{(r_1, \dots, r_\ell) : \sum_{k=1}^{\ell} r_k = \ell u\}$ (up to a multiplicative constant). In particular it follows that

$$\nu(dr_1, \dots, dr_\ell | r_i,\ i \neq 1, \dots, \ell, \mathcal{F}_{inv}) = \frac{e^{-\sum_{i=1}^{\ell}(\hat{\beta}V(r_i) - \hat{\lambda}r_i)}}{Z(\hat{\lambda}, \hat{\beta})^{\ell}} dr_1 \dots dr_\ell.$$

which implies

$$\nu(dr|\mathcal{F}_{inv}) = \prod_{j\in\mathbb{Z}} \frac{e^{-(\hat{\beta}V(r_i) - \hat{\lambda}r_i)}}{Z(\hat{\lambda}, \hat{\beta})} \tag{5.2.11}$$

Similarly, choosing in (5.2.8) the function

$$F = \psi(p)(r_j - z_0)$$

we have

$$0 = \int \left\{(p_j - p_{j-1})\psi(p) + \sum_i \left(V'(r_{i+1}) - V'(r_i)\right)(r_j - z_0)\partial_{p_i}\psi(p)\right\} d\nu(r, p|\mathcal{F}_{inv}) \tag{5.2.12}$$

Since

$$\begin{aligned}\int V'(r_i)(r_j - z_0)\partial_{p_i}\psi(p)\ d\nu(r,p|\mathcal{F}_{inv})\\ = \int d\nu(r|\mathcal{F}_{inv})V'(r_i)(r_j - z_0)\left(\int \partial_{p_i}\psi(p)\nu(dp|\mathcal{F}_{inv})\right)\\ = \delta_{i,j}\hat{\beta}^{-1}\int \partial_{p_i}\psi(p)\ d\nu(p|\mathcal{F}_{inv})\end{aligned}$$

and (5.2.12) became

$$\int \left\{(p_j - p_{j-1})\psi(p) + \beta^{-1}(\partial_{p_j} - \partial_{p_j})\psi(p)\right\}\ d\nu(p|\mathcal{F}_{inv}) = 0 \tag{5.2.13}$$

which is enough to characterise $d\nu(p|\mathcal{F}_{inv})$ as

$$\nu(dp|\mathcal{F}_{inv}) = \prod_{j\in\mathbb{Z}} \frac{e^{-\hat{\beta}(p_i - z_1)^2/2}}{\sqrt{2\pi\hat{\beta}^{-1}}} \tag{5.2.14}$$

and finally we have by lemma 5.2.4

$$\nu(dr, dp|\mathcal{F}_{inv}) = \nu(dr|\mathcal{F}_{inv})\nu(dp|\mathcal{F}_{inv}) = \mu^{gc}_{\mathbf{z}} \tag{5.2.15}$$

□

5.3 Conservative stochastic dynamics

The proof exposed in section 5.2 is based on the assumption that the stationary distribution of the velocity, conditioned on the positions, are convex combination of gaussians. Nowhere we used the non-linearity of the interaction, that in a hamiltonian deterministic dynamics should be the cause of such mixing of velocities. This is a very difficult problem, that we do not even know how to attack mathematically. We choose an easier path here which is to approximate the mixing effect due the non-linearities of the dynamics by adding some stochastic terms to it. The porpouse of this stochastic term is to create this mixing of the velocities so that we can apply the argument of section 5.2. We also would like that the total momentum and total energy is conserved by this stochastic mechanism, and that has a *local* nature. A simple way is to exchange the momentum of each consecutive particles p_j, p_{j+1}, in such way that $p_j + p_{j+1}$ and $p_j^2 + p_{j+1}^2$ are both conserved. Define the exchange operators acting on functions $f : \Omega \to \mathbb{R}$ by

$$(Y_{i,j}f)(r,p) = f(r,p^{j,k}) - f(r,p) \tag{5.3.1}$$

and for consecutive particles

$$Y_i = Y_{i,i+1}$$

We define now the operator

$$\mathcal{S} = \sum_i Y_i \tag{5.3.2}$$

The energy-momentum conservative infinite dynamics is defined as the Markov process on $\Omega = (\mathbb{R}^2)^{\mathbb{Z}}$ generated by the formal generator

$$\mathcal{L} = \mathcal{A} + \gamma \mathcal{S}. \tag{5.3.3}$$

In this section we show the following ergodic property for the infinite stochastic dynamics:

Theorem 5.3.1. *Let ν a translation invariant probability measure, stationary for the dynamics generated by $\mathcal{L}$. Assume that there exist a finite constant C such that*

$$H_\Lambda(\nu|\mu) \le C|\Lambda| \tag{5.3.4}$$

Then ν is a convex combination of grand canonical measures.

The ode describing the evolution are now substiuted by the following stochastic differential equations:

$$\begin{aligned}
dr_j(t) &= p_j(t) - p_{j-1}(t)dt \\
dp_j(t) &= (V'(r_{j+1}(t) - V'(r_j(t)))dt \\
&\quad + \sqrt{\gamma}\,(p_{j+1}(t-) - p_j(t-))\,dN_{j,j+1}(t) + \sqrt{\gamma}\,(p_{j-1}(t-) - p_j(t-))\,dN_{j-1,j}(t), \qquad j \in \mathbb{Z}.
\end{aligned} \tag{5.3.5}$$

where $N(t) = (N_{j,j+1}(t))_{j\in\mathbb{Z}}$ are independent standard Poisson processes.

The existence of the infinite dynamics is done similarly to the deterministic case. To get the approximation by finite dimensional dynamics one defines a dynamics generated by $\mathcal{L}_n = \mathcal{A}_n + \gamma\mathcal{S}_n$, then we prove that this converges to the infinite dynamics in a set of initial conditions that has measure one for any Gibbs measure.

Notice that also here all Gibbs measure with null momentum average are stationary for these finite dynamics.

For the set of initial conditions we choose as in the deterministic case the Hilbert space

$$\Omega_a = \left\{ \omega = (r_j, p_j)_{j\in\mathbb{Z}} \in (\mathbb{R}^2)^{\mathbb{Z}} \ : \ \|\omega\|_a^2 = \sum_{j\in\mathbb{Z}} (p_j^2 + r_j^2) e^{-a|j|} < \infty \right\}, \quad a > 0$$

equipped with the norm $\|\cdot\|_a$. The set Ω_a has measure one with respect to any Gibbs measure. In the following lemma, the expectation $\mathbb{E}$ is the probability measure corresponding to the sequence of independent Poisson processes $N = (N_{j,j+1})_{j\in\mathbb{Z}}$. We also introduce the Banach space $\mathcal{H}_a$ composed of all predictable Ω_a-valued processes ω on the time interval $[0,T]$ with norm

$$N(\omega) = \left[\mathbb{E} \left(\sup_{t\in[0,T]} \|\omega(t)\|_a^2 \right) \right]^{1/2}$$

Lemma 5.3.2. *For any $\sigma \in \Omega_a$, there exists a unique stochastic process $\omega(\cdot,\sigma) = (r_i(\cdot), p_i(\cdot))_{i\in\mathbb{Z}}$ belonging to $\mathcal{H}_a$ and satisfying (5.3.5) with initial condition $\omega(0,\sigma) = \sigma$. The application $\sigma \in \Omega_a \to \omega(\cdot,\sigma) \in \mathcal{H}_a$ is continuously differentiable and the derivatives satisfy the linearized equations associated to (5.3.5).*

Proof The proof relies on the classical iteration procedure in Banach spaces. It is standard and we only sketch the proof. Let us write (5.3.5) in the form

$$d\omega(t) = F(\omega(t))dt + B(\omega(t-))dN(t) \tag{5.3.6}$$

where $F : \Omega_a \to \Omega_a$, $B : \Omega_a \to \Omega_a$ are suitable functions whose exact expression is not used. Using (5.1.1) it is not difficult to see that the map

$$\begin{array}{rcl} \mathcal{K} : \Omega_a \times \mathcal{H}_a & \to & \mathcal{H}_a \\ (\sigma,\omega) & \to & \sigma + \int_0^{\cdot} F(\omega(s))ds + \int_0^{\cdot} B(\omega(s-))dN(s) \end{array}$$

is such that

$$N\left(\mathcal{K}(\sigma,\omega) - \mathcal{K}(\sigma,\omega')\right) \le \frac{1}{2} N(\omega - \omega')$$

if T is sufficiently small. By Picard's fixed point theorem there exists a unique $\omega \in \mathcal{H}_a$ such that $\mathcal{K}(\sigma,\omega) = \omega$. This establish the existence and uniqueness of $\omega(\cdot,\sigma)$ for short time interval. Iterating the procedure gives the existence (and uniqueness) for all times.

To get the differentiability with respect to initial conditions we observe that $\omega(\cdot,\sigma)$ satisfies

$$\mathcal{K}(\sigma,\omega(\cdot,\sigma))-\omega(\cdot,\sigma))=0 \tag{5.3.7}$$

and that local inversion theorem is valid because of the assumption (5.1.1). This implies the claim. □

Starting from an initial configuration $\omega\in\Omega_a$, conservation of the energy by the dynamics gives the following a priori bound

$$\mathbb{E}_\omega\left[\sum_j e^{-a|j|}\mathcal{E}_j(\omega(t))\right]\leq C_0e^{c_1t}\left[\sum_j e^{-a|j|}\mathcal{E}_j(\omega)\right] \tag{5.3.8}$$

By this way we define a semigroup $(P^t)_{t\geq 0}$ on $C_0(\Omega_a)$

$$\forall f\in B(\Omega_a),\ \forall\sigma\in\Omega_a,\quad (P^tf)(\sigma)=\mathbb{E}_\omega\left[f(\omega(t,\sigma)\right]$$

where $\omega(t,\sigma)=\{r_j(t),p_j(t);\ j\in\mathbb{Z}\}$ is the solution of (5.3.5).

By Itô's formula we have that if f is two times differentiable with bounded derivatives then

$$(P^tf)(\sigma)=f(\sigma)+\int_0^t(P^s\mathcal{L}f)(\sigma)ds \tag{5.3.9}$$

Moreover if $f\in C_0^2(\Omega_a)$ and $t\geq 0$ then by lemma 5.3.2 the function $g=P^tf$ is two times differentiable with bounded derivatives. By (5.3.9) we have the forward Kolmogorov equation

$$(P^hg)(\sigma)-g(\sigma)=\int_0^h(P^s\mathcal{L}g)(\sigma)ds$$

and the function $s\to(P^s\mathcal{L}g)(\sigma)$ is continuous because $\omega(\cdot,\sigma)$ has continuous trajectories and $\mathcal{L}g$ is a bounded function. Therefore, sending $h\to 0$, we have

$$\frac{d}{dh}\Big|_{h=0}((P^hg)(\sigma))=\frac{d}{dh}\Big|_{h=t}((P^hf)(\sigma))=(\mathcal{L}g)(\sigma)$$

so that the backward Kolmogorov equation is valid

$$(P^tf)(\sigma)=f(\sigma)+\int_0^t(\mathcal{L}P^sf)(\sigma)ds \tag{5.3.10}$$

Two probability measures μ and ν on Ω such that $\int fd\mu=\int fd\nu$ for all $f\in\mathcal{D}(\Omega)$ are equal. If μ is a stationary state for $(P^t)_t$ then the forward Kolmogorov equation implies that $\int\mathcal{L}fd\mu=0$ for all $f\in\mathcal{D}(\Omega)$. If $\int\mathcal{L}fd\mu=0$ for all $f\in\mathcal{D}(\Omega)$ then the backward Kolmogorov equation implies that $\int(P^tf)d\mu=\int fd\mu$ for every $f\in\mathcal{D}(\Omega)$ and hence μ is stationary for $(P^t)_{t\geq 0}$. Hence we have

Lemma 5.3.3. *Stationary states μ satisfying the moment condition*

$$\sup_{j\in\mathbb{Z}} \int \mathcal{E}_j d\mu < +\infty$$

are characterized by the stationary Kolmogorov equation:

$$\int \mathcal{L}\phi(\omega) d\mu(\omega) = 0 \textit{ for } \phi \in \mathcal{D}(\Omega)$$

We now prove that the infinite volume dynamics is well approximated by the finite dimensional dynamics $\omega^n(t) = \{r_i^n(t), p_i^n(t), i \in \mathbb{Z}\}$. It is defined by the following stochastic differential equations

$$\begin{aligned}
&\dot{r}_i^{(n)}(t) = p_i^{(n)}(t) - p_{i-1}^{(n)}(t) \qquad i = -n, \dots, n+1 \\
&\dot{p}_i^{(n)}(t) = V'(r_{i+1}^{(n)}(t)) - V'(r_i^{(n)}(t)) \\
&\qquad + \mathbf{1}_{\{i\le n-1\}} \sqrt{\gamma}\,(p_{i+1}(t-) - p_i(t-))\, dN_{i,i+1}(t) + \mathbf{1}_{\{i\ge -n+1\}} \sqrt{\gamma}\,(p_{i-1}(t-) - p_i(t-))\, dN_{i-1,i}(t), \\
&\qquad\quad i = -n, \dots, n.
\end{aligned} \tag{5.3.11}$$

with the coordinates $(q_i(t), p_i(t)) = (q_i(0), p_i(0))$ if $i \notin \{-n, \dots, n\}$. The dynamics is generated by $\mathcal{L}_n = \mathcal{A}_n + \mathcal{S}_n$ where $\mathcal{A}_n$ is defined by

$$\mathcal{A}_n = \sum_{j=-n}^{n} \left\{ p_j(\partial_{r_j} - \partial_{r_{j+1}}) + (V'(r_{j+1}) - V'(r_j))\, \partial_{p_j} \right\} \tag{5.3.12}$$

and $\mathcal{S}_n$ is given by

$$\mathcal{S}_n = \sum_{j=-n}^{n-1} Y_j^2 \tag{5.3.13}$$

Remark that (5.3.8) is also valid for the finite-dimensional dynamics

$$\mathbb{E}_\omega\left[\sum_j e^{-a|j|} \mathcal{E}_j(\omega^{(n)}(t))\right] \le C_0 e^{c_1 t} \left[\sum_j e^{-a|j|} \mathcal{E}_j(\omega)\right] \tag{5.3.14}$$

Choose a initial configuration $\omega \in \Omega_a$ and $b > a$. Let us define

$$\delta_n(t) = \mathbb{E}_\omega\left(\|\omega^{(n)}(t) - \omega(t)\|_b^2\right) = \mathbb{E}_\omega\left(\sum_{i\in\mathbb{Z}} e^{-b|i|} \left(|r_i^{(n)}(t) - r_i(t)|^2 + |p_i^{(n)}(t) - p_i(t)|^2\right)\right) \tag{5.3.15}$$

where the dynamics $\omega^{(n)}(t)$ and $\omega(t)$ start from the same initial configuration ω.

By Cauchy-Schwarz's inequality and Itô's formula, we have

$$\delta_n(t) \le C_T \int_0^t ds \delta_n(s) + C_T \sum_{|i|\ge n-2} e^{-b|i|} \mathbb{E}_\omega \left[\mathcal{E}_i(\omega) + \mathcal{E}_i(\omega(t)) + \mathcal{E}_i(\omega^{(n)}(t)) \right], \quad t \in [0,T] \tag{5.3.16}$$

where C_T is a positive constant depending on T and such that C_T goes to zero with T and that can change from line to line. By the a priori bounds (5.3.8, 5.3.14), we have

$$\mathbb{E}_\omega \left[\mathcal{E}_i(\omega) + \mathcal{E}_i(\omega(t)) + \mathcal{E}_i(\omega^{(n)}(t)) \right] \le C_T e^{a|i|} \left(\sum_{j\in\mathbb{Z}} e^{-a|j|} \mathcal{E}_j(\omega) \right) \tag{5.3.17}$$

so that

$$\delta_n(t) \le C_T \int_0^t ds \delta_n(s) + \varepsilon_n, \quad \varepsilon_n \le \frac{C_T}{b-a} e^{-(b-a)n} \left(\sum_{j\in\mathbb{Z}} e^{-a|j|} \mathcal{E}_j(\omega) \right) \tag{5.3.18}$$

By Gronwall's inequality we get

$$\delta_n(t) \le \varepsilon_n e^{C_T T} \tag{5.3.19}$$

Let P_n the semigroup generated by $\mathcal{L}_n$. Estimate (5.3.19) is enough to prove the following lemma

Lemma 5.3.4. *Let $a > 0$ and $\omega \in \Omega_a$, then*

- *$\mathbb{P}_\omega$ a.s., $(r_i^{(n)}(t), p_i^{(n)}(t))$ converges to $(r_i(t), p_i(t))$ as n goes to infinity.*
- *For any bounded Lipschitz local function ϕ and $t \in [0,T]$ there exist constants $C_n = C_n(a,T,\phi) \to 0$ as $n \to \infty$ such that:*

$$\left| P_n^t \phi(\omega) - P^t \phi(\omega) \right| \le C_n \left(\sum_{j\in\mathbb{Z}} e^{-a|j|} \mathcal{E}_j(\omega) \right)$$

Let μ and ν probability measures on $\Omega = (\mathbb{R}^2)^{\mathbb{Z}}$, and for any $\Lambda \subset \mathbb{Z}$ let $\mathcal{F}_\Lambda$ the ensemble of the measurable functions of $\omega_\Lambda = (r_j, p_j; j \in \Lambda)$ (i.e. functions on Ω that depends only on the variables in Λ).

In the following let $\mu = \mu_{\beta_0}^{gc}$ a grandcanonical Gibbs measure at temperature β_0^{-1}. If ν is translation invariant, denoting $\Lambda_n = \{-n, \dots, n\}$, we have that $H_{\Lambda_n}(\nu|\mu)$ is a superadditive function of n (see proposition **??**), and consequently it exists the limit

$$\bar{H}(\nu|\mu) = \lim_{n\to\infty} \frac{1}{2n+1} H_{\Lambda_n}(\nu|\mu) = \sup_n \frac{1}{|\Lambda_n|} H_{\Lambda_n}(\nu|\mu) \tag{5.3.20}$$

For any local measurable function ϕ define the limit

$$\bar{F}(\phi) = \lim_{n\to\infty} \frac{1}{2n+1} \bar{F}_n(\phi), \quad \bar{F}_n(\phi) = \log \int e^{\sum_{i=-n}^{n} \tau_i \phi} \, d\mu \tag{5.3.21}$$

where τ_i is the shift operator on functions on $(\mathbb{R}^2)^{\mathbb{Z}}$.

We recall here proposition **??**:

Proposition 5.3.5. *Let ν a translation invariant probability on Ω, then*

$$\bar{H}(\nu|\mu) = \sup_{\phi} \left\{ \int \phi \, d\nu - \bar{F}(\phi) \right\} \tag{5.3.22}$$

where the supremum is taken over all bounded measurable local functions ϕ.

As a consequence we can prove easily the following bound on the average energy density:

$$\int \mathcal{E}_0 \, d\nu \le C(1 + H_\Lambda(\nu|\mu)) \tag{5.3.23}$$

Here is the ergodic property for the infinite stochastic dynamics:

Theorem 5.3.6. *Let ν a translation invariant probability measure, stationary for the dynamics generated by $\mathcal{L}$. Assume that there exist a finite constant C such that*

$$H_\Lambda(\nu|\mu) \le C|\Lambda| \tag{5.3.24}$$

where $\mu = \mu_{\beta_0}$ is a reference grand canonical measure. Then ν is a convex combination of grand canonical measures.

We have seen that for a translation invariant ν, (5.3.24) is equivalent to the condition $\bar{H}(\nu|\mu) \le C < \infty$.

The proof is divided in two steps. Let us first consider a generic probability mesure ν_*, not necessarily translation invariant, such that $H(\nu_*|\mu) < \infty$, and let us denote by $g = \frac{d\nu_*}{d\mu}$. Let us denote, for any n, the Dirichlet forms:

$$D_n(\nu_*) = \sup_{\psi} \left\{ - \int \frac{\mathcal{S}_n \psi}{\psi} \, d\nu_* \right\} \tag{5.3.25}$$

where the supremum is carried on the set of positive functions $\psi : \Omega \to (0, +\infty)$ such that $0 < M^{-1} \le \psi \le M < +\infty$ for some positive constant M.

Lemma 5.3.7. *Let ν^* be be a probability measure on Ω absolutely continuous w.r.t. μ and such that $D_n(\nu_*) < +\infty$. Then $g = d\nu^*/d\mu$ satisfies*

$$D_n(\nu_*) = \frac{1}{2}\sum_{j=-n}^{n-1} \int (Y_j\sqrt{g})^2 \, d\mu \ . \tag{5.3.26}$$

Proof: Let $\psi : \Omega \to (0, +\infty)$ such that $0 < M^{-1} \le \psi \le M < +\infty$ for some positive constant M. Observe that $Y_i^2 = -2Y_i$ and that Y_i is a self-adjoint operator in $\mathbb{L}^2(\mu)$. Therefore

$$\begin{aligned}
- \ \int \frac{\mathcal{S}_n\psi}{\psi}\, d\nu_* &= \frac{1}{2}\sum_{i=-n}^{n-1}\int \frac{Y_i^2\psi}{\psi} g d\mu = \frac{1}{2}\sum_{i=-n}^{n-1}\int Y_i\psi\, Y_i\left(\frac{g}{\psi}\right)\, d\mu \\
= \ &\frac{1}{2}\sum_{i=-n}^{n-1}\int \left[g(p^{i,i+1}) - g(p^{i,i+1})\frac{\psi(p)}{\psi(p^{i,i+1})} - g(p)\frac{\psi(p^{i,i+1})}{\psi(p)} + g(p)\right] d\mu \\
= \ &\frac{1}{2}\sum_{i=-n}^{n-1}\int \left[g(p^{i,i+1}) - \sqrt{g}(p^{i,i+1})\sqrt{g}(p)\left[\frac{(\psi/\sqrt{g})(p)}{(\psi/\sqrt{g})(p^{i,i+1})} + \frac{(\psi/\sqrt{g})(p^{i,i+1})}{(\psi/\sqrt{g})(p)}\right] + g(p)\right] d\mu \\
\le \ &\frac{1}{2}\sum_{j=-n}^{n-1}\int (Y_j\sqrt{g})^2\, d\mu
\end{aligned}$$

because $z + 1/z \ge 2$ for every positive z. This proves $D_n(\nu^*) \le \frac{1}{2}\sum_{j=-n}^{n-1}\int (Y_j\sqrt{g})^2\, d\mu$.

For the other sense of the inequality, let $M > 0$ and consider $\psi_M = M^{-1} + \inf(\sqrt{g}, M)$. We have seen that

$$D_n(\nu^*) \ge \frac{1}{2}\sum_{i=-n}^{n-1}\int \left[g(p^{i,i+1}) - g(p^{i,i+1})\frac{\psi_M(p)}{\psi_M(p^{i,i+1})} - g(p)\frac{\psi_M(p^{i,i+1})}{\psi_M(p)} + g(p)\right] d\mu$$

Observe that $\dfrac{\psi_M(p^{i,i+1})}{\psi_M(p)}$ is positive and converges to $\sqrt{g}(p^{i,i+1})/\sqrt{g}(p)$. By Fatou lemma we get

$$D_n(\nu_*) \ge \frac{1}{2}\sum_{j=-n}^{n-1}\int (Y_j\sqrt{g})^2\, d\mu$$

which completes the proof. □

A simple consequence of proposition **??** and convexity of the Dirichlet form gives the following

Proposition 5.3.8. *For any probability mesure ν and any n, we have*

$$H(\nu_* P_n^t|\mu) + tD_n(\bar{\nu}_{*,n}^t) \leq H(\nu_*|\mu) \tag{5.3.27}$$

where $\bar{\nu}_{*,n}^t = t^{-1}\int_0^t \nu_* P_n^s ds$.

Because of (5.3.26), if $H(\nu_*|\mu) < +\infty$, then for any $j = -n+1, \ldots, n-1$

$$H(\nu_* P_n^t|\mu) + \frac{t}{2}\sum_{j=-n}^{n-1}\int (Y_j\sqrt{\bar{g}_n^t})^2 \, d\mu \leq H(\nu_*|\mu)$$

where $\bar{g}_n^t = \frac{d\bar{\nu}_{*,n}^t}{d\mu}$. In the second term of the above, because is composed by a sum of positive parts, we can restrict this to any $m \leq n-1$:

$$H(\nu_* P_n^t|\mu) + \frac{t}{2}\sum_{j=-m}^{m}\int (Y_j\sqrt{\bar{g}_n^t})^2 \, d\mu \leq H(\nu_*|\mu)$$

By (**??**) and (5.3.25), for any choice of function $\phi \in \mathcal{D}(\Omega)$ and local functions $\psi_i \in \mathcal{D}(\Omega)$ (bounded by below by a positive constant)

$$\int P_n^t\phi \, d\nu_* - \log\int e^{\phi}d\mu - \frac{t}{2}\sum_{j=-m}^{m}\int \frac{Y_i^2\psi_i}{\psi_i}\, d\bar{\nu}_{*,n}^t \leq H(\nu_*|\mu)$$

Now we can finally let $n \to \infty$, and by theorem 5.3.4 we obtain

$$\int P^t\phi \, d\nu_* - \log\int e^{\phi}d\mu - \frac{t}{2}\sum_{j=-m}^{m}\int \frac{Y_i^2\psi_i}{\psi_i}\, d\bar{\nu}_{*}^t \leq H(\nu_*|\mu) \tag{5.3.28}$$

where $\bar{\nu}_*^t = t^{-1}\int_0^t \nu_* P^s \, ds$.

Proposition 5.3.9. *Let ν be a translation invariant measure stationary for P^t such that for a finite constant C, $H_\Lambda(\nu|\mu_{\beta_0}^{gc}) \leq C|\Lambda|$ for any finite interval Λ. Then for any n we have $D_n(\nu) = 0$.*

Proof We apply now (5.3.28) to $\nu_* = \nu_*^{(m)} = \nu|_{\Lambda_m} \otimes \mu|_{\Lambda_m^c}$. Notice that $H(\nu_*^{(m)}|\mu) = H_{\Lambda_m}(\nu|\mu)$, and consequently

$$\lim_{m\to\infty}\frac{1}{2m}H(\nu_*^{(m)}|\mu) = \bar{H}(\nu|\mu)$$

Choosing $\phi = \sum_{i=-m}^m \tau_i\phi_0$, $\psi_i = \tau_i\psi_0$, where $\phi_0 \in \mathcal{D}(\Omega)$ and $\psi_0 \in \mathcal{D}(\Omega)$ is bounded by below by a positive constant, we obtain

$$\sum_{i=-m}^{m}\int P^t(\tau_i\phi_0)\, d\nu_*^{(m)} - \bar{F}_m(\phi_0) - \frac{t}{2}\sum_{i=-m}^{m}\int \tau_i\frac{Y_0^2\psi_0}{\psi_0}\, d\bar{\nu}_*^{(m),t} = H(\nu_*^{(m)}|\mu)$$

and all we need to prove is that

$$\lim_{n\to\infty}\frac{1}{2n+1}\sum_{i=-n}^{n}\int P^t(\tau_i\phi_0)\ d\nu_*^{(n)}=\int P^t\phi_0 d\nu=\int\phi_0 d\nu \tag{5.3.29}$$

and

$$\lim_{n\to\infty}\frac{1}{2n+1}\sum_{i=-n}^{n}\int\tau_i\frac{Y_0^2\psi_0}{\psi_0}\ d\bar{\nu}_*^{(n),t}=\int\frac{Y_0^2\psi_0}{\psi_0}\ d\nu \tag{5.3.30}$$

In fact maximising what we obtained over ϕ_0 and ψ_0 we get

$$-\inf_{\psi_0}\int\frac{Y_0^2\psi_0}{\psi_0}\ d\nu=0$$

It is clear that we can repeat the argument substituting Y_j to Y_0, and we obtain

$$-\inf_{\psi_0}\int\frac{Y_j^2\psi_0}{\psi_0}\ d\nu=0$$

In the last infimum it is easy to extend the infimum to the set of functions $\psi_0:\Omega\to(0,+\infty)$ bounded by above and by below by positive constants. Summing up over j we obtain

$$0\le D_n(\nu)=-\inf_{\psi}\sum_{j=-n-1}^{n+1}\int\frac{Y_j^2\psi}{\psi}\ d\nu\le-\sum_{j=-n-1}^{n+1}\inf_{\psi}\int\frac{Y_j^2\psi}{\psi}\ d\nu=0.$$

□

Proof of (5.3.29) and (5.3.30).

The difficulty comes form the fact that $P^t\phi$ is not local.

We approximate again P^t by our local dynamics P^t_ℓ. Observe that by (5.3.23), for any $i=1,\dots,n$,

$$\int\mathcal{E}_j(\omega)d(\tau_i\nu_*^{(n)})\le\sup_{i\in\mathbb{Z}}\left(\int\mathcal{E}_i d\nu+\int\mathcal{E}_i d\mu\right)\le K$$

with K independent of n. Then it follows from lemma 5.3.4 that

$$\sup_n\left|\int P^t\phi\ d(\tau_i\nu_*^{(n)})-\int P^t_\ell\phi\ d(\tau_i\nu_*^{(n)})\right|\le KC_\ell\sum_{j\in\mathbb{Z}}e^{-a|j|}$$

with $C_\ell\to 0$ as $\ell\to\infty$.

Now we have that $P^t_\ell \phi$ is a local function, and by definition of $\nu_*^{(n)}$,

$$\frac{1}{2n+1}\sum_{i=-n}^{n}\int P^t_\ell\phi\; d(\tau_i\nu_*^{(n)}) = \frac{1}{2n+1}\sum_{i=-n}^{n}\int P^t_\ell\phi\; d(\tau_i\nu) + C(\ell)/n$$

for some constant $C(\ell) > 0$. Sending first n to infinity and then ℓ we get

$$\lim_{\ell\to\infty}\lim_{n\to\infty}\frac{1}{2n+1}\sum_{i=-n}^{n}\int P^t_\ell\phi\; d(\tau_i\nu_*^{(n)}) = \int P^t\phi\; d\nu = \int \phi d\nu.$$

Proof of (5.3.30) is similar.

□

Theorem 5.3.6 is a consequence of the following proposition

Proposition 5.3.10. *If ν is a probability measure on Ω such that $H_\Lambda(\nu|\mu) \le C|\Lambda|$ for every finite subset Λ and satisfying $D_n(\nu) = 0$ for any $n \ge 2$, then $\nu(dp|r)$ is exchangeable.*

Proof Let g_n be the density of $\nu|_{\Lambda_n}$ with respect to $\mu|\Lambda_n$ where $\Lambda_n = \{-n, \dots, n\}$. We call $\mathcal{B}_n$ the set of functions $\psi(r,p)$ bounded by below and by above by strictly positive constants and depending on the p's only through $p_i, i \in \Lambda_n$.

The condition $D_n(\nu) = 0$ implies

$$0 = \sup\left\{-\int \frac{\mathcal{S}_n\psi}{\psi} d\nu|_{\Lambda_n}\ ;\ \psi\in\mathcal{B}_n\right\} \tag{5.3.31}$$

The proof of lemma 5.3.7 shows that the right hand side is equal to

$$\frac{1}{2}\sum_{j=-n}^{n-1}\int \left(Y_j\sqrt{g_n}\right)^2 d\mu|_{\Lambda_n} \tag{5.3.32}$$

Since the sum is composed of positive terms it implies that $g_n(r, p^{j,j+1}) = g_n(r,p)$ a.s. for every $j \in \{-n, \dots, n-1\}$. Since this is true for every $n \ge 2$ we get that $\nu(dp|r)$ is exchangeable.

□

We conclude the proof of Theorem 5.3.6, by observing that ν is separately stationary for $\mathcal{S}$ and $\mathcal{A}$, and then we conclude by applying Theorem 5.2.3.

5.4 Other stochastic dynamics

5.4.1 Energy conserving noise

We can also define a noise $\mathcal{S} = \sum_j X_j^2$ acting on the momenta conserving only kinetic energy. The construction is similar : for nearest neighbors atoms $j, j+1$ we define the vector field X_j by

$$X_j = p_{j+1}\partial_{p_j} - p_j\partial_{p_{j+1}} \tag{5.4.1}$$

It is tangent to the circle $\{(p_j, p_{j+1}) \in \mathbb{R}^2; \quad p_j^2 + p_{j+1}^2 = 1\}$ so that

$$\mathcal{S} = \sum_j X_j^2 \tag{5.4.2}$$

conserves the kinetic energy. Momentum is not conserved and is in fact eigenvector of $\mathcal{S}$ since $\mathcal{S}(p_j) = -p_j$.

5.4.2 Momentum exchange and momentum flip

One can also consider noise of Poissonian type conserving energy and eventually also momentum. Poissonian energy conserving noise is defined by the following flip operator

$$(\mathcal{S}f)(p) = \sum_j \left[f(p^j) - f(p)\right] \tag{5.4.3}$$

where p^j is the configuration obtained from p by changing the coordinate p_j in $-p_j$.

Poissonian momentum-energy conserving noise is realized by exchange of momenta of nearest neighbor atoms. The generator of this noise is given by

$$(\mathcal{S}f)(p) = \sum_j \left[f(p^{j,j+1}) - f(p)\right] \tag{5.4.4}$$

where $p^{j,j+1}$ is the configuration obtained from p by exchanging the coordinates p_j and p_{j+1}.

Remark that these noise have very poor ergodic properties (which is not the case of the Brownian noises defined before). Nevertheless results of section 5.2 can be applied for them and it implies that the dynamics obtained by adding these noises to the Hamiltonian dynamics is ergodic.

5.5 Bibliographical Notes

The argument for the proof of the ergodicity of the stochastic model is adapted from [14], [12], [**?**] and [7].

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