Thermodynamics, Statistical Mechanics and Large Deviations

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Course Notes

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Chapter 1

Thermodynamics: a crash course

1.1 Thermodynamic equilibrium states

From a mechanical point of view, the *equilibrium* state of an elastic wire is characterized by its *length* $\mathcal{L}$, that can be changed applying a *tension* (force) τ on the extremes. The resulting length is an increasing function of τ: $\mathcal{L} = F(\tau)$. We also observe that this function F depends also on the *temperature* θ of the wire, typically increasing with θ. The first object of thermodynamics is to introduce this parameter θ, whose definition (or measurement) is much more delicate than $\mathcal{L}$ or τ.

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

> *If a system A remains in equilibrium when isolated and placed in thermal contact first with system B and then with system C, the equilibrium of B and C will not be disturbed when they are placed in contact with each other.*

Here *"remains in equilibrium"* means that the relation between $\mathcal{L}$ and τ does not change. We also use here the concept of *isolated system* and *thermal contact*, that require respectively the notion of adiabatic wall and conductive wall.

The system A and B are separated by an *adiabatic wall* if they can have different equilibrium relation between $\mathcal{L}$ and τ. They are separated by a *conductive wall* if the must have the same equilibrium relation.

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

One could see all these as circular definition, in fact all this is equivalent as postulating the existence of adiabatic and diathermic (thermally conductive) walls that are defined as devices that have the above properties. From all this we obtain the existence of the parameter θ that we call temperature (see in Zemanski a very detailed discussion of this point).

So we can define the equilibrium relation $\mathcal{L} = \mathcal{L}(\tau, \theta)$. Since it is strictly increasing in both variable we can also write $\tau = \tau(\mathcal{L}, \theta)$, as well as $\theta = \theta(\mathcal{L}, \tau)$, i.e. any two of these three variables can be chosen independently in order to characterize a thermodynamic equilibrium state.

1.2 Differential changes of equilibrium states

Suppose we have our wire in the thermodynamic equilibrium defined by the value τ, θ. This can be obtained by applying a tension τ to one extreme and fixing the other to a wall, 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 lenght:

$$d\mathcal{L} = \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_\tau d\theta + \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_\theta d\tau \tag{1.2.1}$$

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

- the *linear dilation coefficient:*

$$\alpha = \frac{1}{\mathcal{L}} \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_\tau \tag{1.2.2}$$

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

- the *isothermal Young modulus*

$$Y = \frac{\mathcal{L}}{A} \left(\frac{\partial \tau}{\partial \mathcal{L}}\right)_\theta \tag{1.2.3}$$

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

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

It is an elementary exercise to prove that

$$\left(\frac{\partial \tau}{\partial \mathcal{L}}\right)_\theta \left(\frac{\partial \mathcal{L}}{\partial \theta}\right)_\tau = -\left(\frac{\partial \tau}{\partial \theta}\right)_\mathcal{L} \tag{1.2.4}$$

and consequently

$$\left(\frac{\partial \tau}{\partial \theta}\right)_\mathcal{L} = -\frac{\alpha}{C_\theta} \tag{1.2.5}$$

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

$$d\tau = \left(\frac{\partial \tau}{\partial \theta}\right)_\mathcal{L} d\theta + \left(\frac{\partial \tau}{\partial \mathcal{L}}\right)_\theta d\mathcal{L} = -\frac{\alpha}{C_\theta} d\theta + \frac{1}{C_\theta \mathcal{L}} d\mathcal{L} \tag{1.2.6}$$

At constant volume we have

$$d\tau = -\frac{\alpha}{C_\theta} d\theta \tag{1.2.7}$$

One of the main issues in discussing foundations of thermodynamics is the physical meaning of these differential changes of *equilibrium* states. In principle, 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 Zemanski, *thermodynamics does not attempt to deal with any problem involving the rate at which the process takes place.* And, always quoting Zemanski:

> 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.

1.2.1 Work

In an arbitrary *quasi static* infinitesimal transformation, the differential form $\tau d\mathcal{L}$ is called *work* (or differential work). It is clear that this is not an exact differential form, but in thermodynamics books it is used the notation $đW$. This 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*, maybe through a sequence of isobar and isocore transformations, the path integral $\oint đW \neq 0$ (equal to the area inside the path), and represent the work done on the system by the external force (tension)[2].

[2]Mathematically the difference with the notion of work in mechanics is that here the force τ is also a function of the temperature

1.2.2 Internal Energy and Heat exchange

The point of the **first principle of thermodynamics** is to preserve the mechanical notion of energy as a conserved quantity also during thermodynamic transformations, which means to **assume** the existence of a state function $U(\mathcal{L}, \theta)$ that represent the internal energy of the system in the corresponding thermodynamic equilibrium state. During a quasi-static thermodynamic infinitesimal transformation, this energy is modified by the work $đW$ and, since dU has to be an exact differential, by some other (not exact) differential form $đQ$ called *heat exchange*:

$$dU = \tau d\mathcal{L} + đQ \tag{1.2.8}$$

It is important to notice that *work* and *heat* are determined by specifying the process of change, and they are not functions of the state of the system. Mathematically this means they are not exact differentials. 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 (that will be the scope of statistical mechanics), this will be the following. The system has many (a very large number) degrees of freedom and many external forces acting on them. Some, few, of these forces are *controlled*, *ordered*, *macroscopic* and *slow*, and the work done by these we still call it **work**, in our case τ is this ordered and controlled slow force, and $\tau d\mathcal{L}$ 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**.

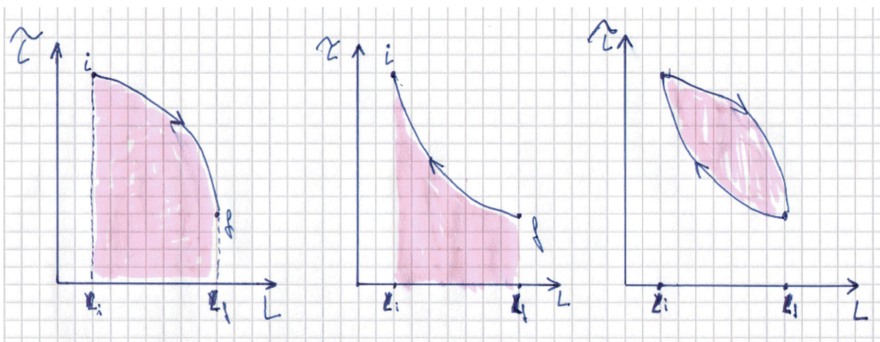
One of the main problem of the statistical mechanic interpretation of thermodynamics is to separate the slow macroscopic degree of freedom that generate work from the fast microscopic ones that generate heat. The slow degrees of freedom are generally associated to conserved quantities of the isolated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

So the first principle (1.2.8) defines this separation of scales (in space and in time), whose mechanical explanation impose the use of probability to describe the uncontrolled forces.

1.2.3 Thermodynamic transformations and cycles

We can represent a finite thermodynamic transformation by integration along path of the differential forms defined above. 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 to represent it graphically.

Often is used the $\tau - L$ diagrams.



The first diagram on the left describe a quasi-static transformation for lenght L_i to L_f. If this is happening for example as a free expansion means that the tension τ is decreasing, but it could be increasing if instead τ is pulling with respect the mechanical equilibrium. 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 work is given by the integral along the cycle

$$\Delta W = \oint \tau dL \tag{1.2.9}$$

that by the first principle will be equal to $-\Delta Q$, where ΔQ 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).

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 *thermostat*, a **huge** system in equilibrium at a given temperature θ, so big that the exchange of heat with our elastic does not perturb the equilibrium state of the thermostat. Ideally a thermostat is an infinite system. 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

$$đW = \tau d\mathcal{L} = \tau \left(\frac{\partial \mathcal{L}}{\partial \tau}\right)_\theta d\tau = -đQ + dU \tag{1.2.10}$$

The isothermal transformations defines isothermal lines parametrized by the temperature (each temperature defines an isothermal line in the $\tau - \mathcal{L}$ plane.

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

$$đW = \tau d\mathcal{L} = dU \tag{1.2.11}$$

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

$$\frac{d\tau}{d\mathcal{L}} = -\frac{\partial_{\mathcal{L}}U}{\partial_{\tau}U} \tag{1.2.12}$$

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

$$đQ = dU \tag{1.2.13}$$

- *Isobar transformations*: Thermodynamic transformation at fixed tension $\mathcal{L}$, $d\tau = 0$

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 that generates work from the heat difference of two thermostats. SO different Carnot cycles can be composed in a sequence etc.

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. let us assume that $\theta_2 > \theta_1$. We assume that A and C are in the same adiabatic curve, so are B and D. We perform an (hot) isothermal transformation from A to B, then and adiabatic from B to D, then an (cold) isothermal from D to C, then another adiabatic from C to A.

During the isothermal extension of the wire from A to B, it absorb 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 DC. 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 $Q_2 - Q_1$. By the first principle this is equal to the work done by the system τ:

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

So, unless $Q_1 = 0$, not all heat absorbed from the hot thermostat is changed in work. We define the efficiency of the Carnot cycle:

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

The cycle is reversible, i.e. we can do all the operations in the reverse order. In this case the wire absorbs the work W, the quantity Q_1 is adsorbed by he system at the cold temperature θ_1 and Q_2 is given to the hot thermostat θ_2. So in the reversed cycle is able to move heat from the cold thermostat to the hot, by absorbing a work W.

1.2.4 Second Principle and Entropy

The second principle of thermodynamics has equivalent statements in terms of a Carnot machine.

We enunciate first the Lord Kelvin statement of the second law:

$$\text{if} \quad W > 0, \quad \text{then} \quad Q_2 > 0 \quad \text{and} \quad Q_1 > 0. \tag{1.2.14}$$

Equivalently $\eta < 1$. More prosaically we say that all thermodynamic cycles that transforms all heat extracted from the hot reservoir in work are impossible.

The Clausius statement of the second law is

$$\text{if} \quad W = 0, \quad \text{then} \quad Q_2 = Q_1 > 0. \tag{1.2.15}$$

i.e. it does not exists a cyclic thermodynamic transformation whose only result is a transfer of heat from the cold reservoir to the hot reservoir.

It can be proven that this two statements are equivalent.

The Kelvin postulate (1.2.14) has a simple and intuitive statement, but a very deep consequence: it imply the existence of an absolute scale of *temperature*.

Proposition 1.2.1 *There exists a universal function f such that for* ***any*** *Carnot cycle*

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2) \tag{1.2.16}$$

Proof of proposition 1.2.1.

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

$$\frac{Q_2}{Q_1} = \frac{Q'_2}{Q'_1} \tag{1.2.17}$$

Assume first that the ratio $\frac{Q_2}{Q'_2}$ is a rational number $\frac{N'}{N}$, so that $N'Q'_2 - NQ_2 = 0$. Let us assume that it is null. 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

$$Q_{2,tot} = N'Q'_2 - NQ_2 = 0 \tag{1.2.18}$$

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

$$W_{tot} = -Q_{1,tot} = -(N'Q'_1 - NQ_1) \tag{1.2.19}$$

By the Kelvin postulate we must have $W \leq 0$, that implies

$$N'Q'_1 \geq NQ_1 \tag{1.2.20}$$

that implies

$$\frac{Q_2}{Q_1} \geq \frac{Q'_2}{Q'_1} \tag{1.2.21}$$

To obtain the opposite inequality, we have just to exchange the role of the two machines. The equality (1.2.17) 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 $\frac{Q_2}{Q'_2} = \alpha$ is not rational[3]. 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 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

$$0 < \alpha - \frac{N_k}{N'_k} < \frac{1}{N'_k N'_{k-1}} \tag{1.2.22}$$

This implies $N'_k Q'_2 - N_k Q_2 > 0$. Now we let run the second cycle N'_k times and the first cycle N_k times in the reverse direction. Consequently, by Lord Kelvin statement (1.2.14), we have $Q_1, Q'_1, Q_2, Q'_2 > 0$.

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

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

[3]This argument was suggested by Tomasz Komorowski

By (1.2.22), $N'_k Q'_2 - N_k Q_2 \to 0$ as $k \to \infty$. By the Lord Kelvin statement (1.2.14), $N'_k Q'_1 - N_k Q_1 > 0$, and we obtain

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

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

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. □

Proposition 1.2.2 *For every $\theta_0, \theta_1, \theta_2$, we have*

$$f(\theta_1, \theta_2) = \frac{f(\theta_0, \theta_2)}{f(\theta_0, \theta_1)} \tag{1.2.23}$$

Proof of (1.2.23) : Let A_1 and A_2 two Carnot cycles working respectively between temperature θ_1 and θ_0 and θ_2 and θ_0. Assume that they are chosen in such a way that the amount of heat that they exchange with the thermostat at temperature θ_0 are equal, and we denote it by Q_0. Then A_1 also 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:

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

and we deduce that

$$\frac{Q_1}{Q_2} = \frac{f(\theta_0, \theta_1)}{f(\theta_0, \theta_2)} \tag{1.2.24}$$

But combining the two cycles in sequance, we obtain a cycle that exchange Q_1 with the thermostat at temperature θ_1, and Q_2 to the thermostat at temperature θ_2 (the total heat exchanged with the thermostat θ_0 is null). Consequently for this composite cycle we have

$$\frac{Q_2}{Q_1} = f(\theta_1, \theta_2) \tag{1.2.25}$$

Combining (1.2.23) and (1.2.25) we obtain (1.2.23). □

It follovs 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 $(C_0, F_0$ 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 $\frac{\delta Q}{T}$, this means

$$\oint \frac{\delta Q}{T} = 0 \tag{1.2.26}$$

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), (1.2.26) is actually valid for any cycle, i.e. any closed curve on the state space. Consequently $\frac{\delta Q}{T}$ is an exact form, i.e. the differential of a function S of the state of the system. This function is called Thermodynamic Entropy. [4]

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

$$dS = -\frac{\tau}{T}\, d\mathcal{L} + \frac{1}{T} dU \tag{1.2.27}$$

i.e.

$$\frac{\partial S}{\partial \mathcal{L}} = -\frac{\tau}{T}, \qquad \frac{\partial S}{\partial U} = \frac{1}{T} \tag{1.2.28}$$

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

$$dU = \tau d\mathcal{L} + T dS \tag{1.2.29}$$

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.

[4] 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.

Irreversible transformations

We have worked until here with *reversible* thermodynamic transformations, that can be decribed as quasistatic transformation and by continuous lines of the state space. Actually these *reversibility* is only an idealization. All transformations have to move from an equilibrium state to another, passing through some *non equilibrium state* that the thermodynamics does not attempt to describe. Still thermodynamics, in particular the second principle, can say something about the change of the entropy S when the system goes through non-equilibrium states in passing from an equilibrium to another. These transformations are not time reversible.

A reversible transformation, as the ones we have considered until now, is an ordered succession of equilibrium states. It is quasi static, in the sense that does not take into consideration the time taken by the system to *relax* to these equilibrium states after each change. We can represent it as a line in the state space.

A **real** irreversible transformation is a *temporal* succession of equilibrium and non-equilibrium states. Still taking into account only the equilibrium points, one can represent these irreversible transformations as lines in the (equilibrium) states space. But *the identification of* $\tau d\mathcal{L}$ *as the mechanical work and of* TdS *as the heat transfer is valid only for (reversible) quasi static processes.*

1.3 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 lenght $\mathcal{L}$, 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.

1.4 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 is assumed as a state function satisfying certain properties.

axiom-1) There exist an open cone set $\Gamma \subset \mathbb{R}_+ \times \mathbb{R}$, and $(U, \mathcal{L}) \in \Gamma$.

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:

$$S(\lambda U, \lambda \mathcal{L}) = \lambda S(U, \mathcal{L}), \qquad \lambda > 0 \tag{1.4.1}$$

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

We call

$$\begin{aligned} T &= \frac{\partial U}{\partial S} \qquad \text{temperature} \\ \tau &= \frac{\partial U}{\partial \mathcal{L}} \qquad \text{tension} \end{aligned} \tag{1.4.2}$$

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

One can use also the intensive quantities τ, T as thermodynamic coordinates, and it is useful to define the *Gibbs potential* (also called *free enthalpy*):

$$\begin{aligned} G(T, \tau) &= \inf_{S, \mathcal{L}} \{U(S, \mathcal{L}) - \tau \mathcal{L} - TS\} \\ &= \inf_{U, \mathcal{L}} \{U - \tau \mathcal{L} - TS(U, \mathcal{L})\} \end{aligned} \tag{1.4.3}$$

Exercice:

$$S(U, \mathcal{L}) = \inf_{\tau, T} \left\{ \frac{1}{T} U - \frac{\tau}{T} \mathcal{L} - \frac{G(T, \tau)}{T} \right\} \tag{1.4.4}$$

The differential forms $đQ = TdS$ is called *heating*, and $\tau d\mathcal{L}$ *work*, that imply

$$đQ = -\tau d\mathcal{L} + dU \tag{1.4.5}$$

Thermodynamic transformations that are quasistatic and reversible, and the corresponding *cycles* are then defined as in the previous sections, and the corresponding work and heat exchange as integrals of hese diferential forms on the corresponding lines defining the transformations.

More controversial is the definition of the *non-reversible* transformations. These are *real* thermodynamic transformations that take into consideration the fact that the system, in order to go from one equilibrium state to another, has to pas through *non-equilibrium states.* Without some theory, or modeling, of these non-equilibrium states, all definitions of these *non-reversible* transformations remain vague.

1.4.1 Extended thermodynamics: extended systems

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 the same *mass*), 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 $S(U_1, \mathcal{L}_1) + S(U_2, \mathcal{L}_2)$. Notice that concavity and homogeneity properties of S imply

$$S(U_1, \mathcal{L}_1) + S(U_2, \mathcal{L}_2) \leq 2S\left(\frac{U_1 + U_2}{2}, \frac{\mathcal{L}_1 + \mathcal{L}_2}{2}\right) = S(U_1 + U_2, \mathcal{L}_1 + \mathcal{L}_2) \quad (1.4.6)$$

This means that the composed wire, if 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 lenght (*isocore transformation*, 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 strictly related to the property of this transformation to bring the system towards a global equilibrium.

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

$$\mathcal{L}(x) = \int_0^x r(x')dx' \quad (1.4.7)$$

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

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

$$\mathcal{L}_{tot} = \int_0^1 r(x)dx, \quad U_{tot} = \int_0^1 U(x)dx, \quad S_{tot} = \int_0^1 S(U(x), r(x))dx. \tag{1.4.8}$$

By concavity of S:

$$S_{tot} \leq S(U_{tot}, \mathcal{L}_{tot}) \tag{1.4.9}$$

Usual thermodynamics does not worry about time scales where the thermodynamic processes happens. But in the extended thermodynamics we can consider time evolutions of these profiles (typically evolving following some partial differential equations). The actual time scale in which these evolution occuors with respect to the microscopic dynamivcs 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 correponding time derivatives, we have for the time evolution of the entropy:

$$\partial_t S(U(x,t), r(x,t)) = \frac{1}{T}\left(\dot{U} - \tau \dot{r}\right) \tag{1.4.10}$$

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

$$\begin{aligned} \partial_t r &= \partial_x \pi \\ \partial_t \pi &= \partial_x \tau \\ \partial_t U &= \partial_x(\tau\pi) - \pi\partial_x\tau = \tau\partial_x\pi \end{aligned} \tag{1.4.11}$$

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 $\tau(U(x,t), \mathcal{L}(x,t))$ is the force acting on the material element x (more precisely the gradient $\partial_x \tau$, 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* $\tau\pi$, more precisely by its gradient:

$$\partial_t \mathcal{E} = \partial_x(\tau\pi) \tag{1.4.12}$$

In particular $\partial_t S(U(x,t), r(x,t)) = 0$, i.e. if the solution is C^1, even the entropy is conserved also locally (in the sense that the entropy per component remains unchanged).

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 (3.4.3) is a non-linear hyperbolic system of equation. It is expected that any nontrivial solution will develop shocks. After appeareance of shock, the equations should be considered in a weak sense and a criterion of choice of the weal soluton is that it should have a *positive* production of entropy. A mathematical theorem that guarantee uniqueness of this entropy solution is still lacking. Eventually shocks will create dissipations ans the entropy solution, as $t \to \infty$ will converge to flat profiles for the conserved quantities, i.e. to the system in *global* equilibrium.

Isothermal evolution: diffusion equation

Consider our wire immersed in a viscous liquid at temperature T uniform, that acts as a thermostat on each element x of the wire. 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 onder the constraint that temperature T is constant in x. Velocities of the wire are damped to 0 and it turns out that the evolution is given by the nonlinear diffusion equation:

$$\partial_t r(x,t) = \partial_x^2 \bar{\tau}(x,t) \tag{1.4.13}$$

where $\bar{\tau}(x,t) = \tau(r(x,t), T)$, the tension as function of the lenght and temperature.

Since

$$\partial_t U(x,t) = \frac{\partial U}{\partial \mathcal{L}} \partial_t r \tag{1.4.14}$$

Chapter 2

Large Deviations

2.1 Introduction

As Dembo and Zeitouni point out in the introduction to their monograph on the subject [1], there is no real theory of large deviations, but a variety of tools that allow analysis of small probability.

To give an idea of what we mean with *large deviations*, let us consider a sequence of independent identical distributed real valued random variables $X_1, X_2, \ldots, X_n$ such that $\mathbb{E}(X_j^2) = 1$, and $\mathbb{E}(X_j) = 0$. Let $\hat{S}_n = \frac{1}{n}\sum_i X_i$ the empirical sum. The weak law of large numbers says that for any $\delta > 0$,

$$\mathbb{P}(|\hat{S}_n| \geq \delta) \underset{n\to\infty}{\longrightarrow} 0 \tag{2.1.1}$$

The central limit theorem is a refinement that says

$$\mathbb{P}(\sqrt{n}\hat{S}_n \in [a,b]) \underset{n\to\infty}{\longrightarrow} \frac{1}{\sqrt{2\pi}}\int_a^b e^{-x^2/2}dx \ . \tag{2.1.2}$$

In the case $X_j \sim \mathcal{N}(0,1)$, we have $\hat{S}_n \sim N(0, 1/n)$, and we can compute explicitly

$$\mathbb{P}(|\hat{S}_n| \geq \delta) \ = 1 - \frac{1}{\sqrt{2\pi}}\int_{-\delta\sqrt{n}}^{\delta\sqrt{n}} e^{-x^2/2}dx \ .$$

therefore (**exercise**)

$$\frac{1}{n}\log\mathbb{P}(|\hat{S}_n| \geq \delta) \underset{n\to\infty}{\longrightarrow} -\frac{\delta^2}{2} \tag{2.1.3}$$

Equation (2.1.3) is an example of a large deviation statement.

2.2 Cramér's Theorem in $\mathbb{R}$

Let $\{X_n\}$ a sequence of i.i.d. random variables on $\mathbb{R}$ with common probability distribution $\alpha(dx)$. We define the moment generating function

$$M(\lambda) = \mathbb{E}\left[e^{\lambda X_1}\right] \tag{2.2.1}$$

and let us assume that there exists $\lambda^* > 0$ such that $M(\lambda) < \infty$ if $|\lambda| < \lambda^*$. Notice that, since $|x| \leq \lambda^{-1}(e^{\lambda x} + e^{-\lambda x})$ for any $\lambda > 0$, this condition implies that X_1 is integrable and we denote $m = \mathbb{E}(X_1) \in \mathbb{R}$. It is easy to see that $m = M'(0)$. We are interested in the *logarithmic moment generating function*

$$\mathcal{Z}(\lambda) = \log \mathbb{E}\left[e^{\lambda X_1}\right] \tag{2.2.2}$$

By Jensen's inequality, we have $\mathcal{Z}(\lambda) \geq \lambda m > -\infty$. Let $\mathcal{D}_{\mathcal{Z}} = \{\lambda : \mathcal{Z}(\lambda) < +\infty\}$. Under our hypothesis, $0 \in \mathcal{D}^o_{\mathcal{Z}}$ (the interior of $\mathcal{D}_{\mathcal{Z}}$).

Lemma 2.2.1 *1. $\mathcal{Z}(\cdot)$ is convex.*

2. $\mathcal{Z}(\cdot)$ is continuously differentiable in $\mathcal{D}^o_{\mathcal{Z}}$ and

$$\mathcal{Z}'(\lambda) = \frac{\mathbb{E}(X_1 e^{\lambda X_1})}{M(\lambda)} \qquad \lambda \in \mathcal{D}^o_{\mathcal{Z}}.$$

Proof:

1. For any $\alpha \in [0,1]$, it follows by Hölder inequality

$$\mathbb{E}(e^{(\alpha\lambda_1 + (1-\alpha)\lambda_2)X_1}) \leq M(\lambda_1)^\alpha M(\lambda_2)^{1-\alpha}$$

and consequently

$$\mathcal{Z}(\alpha\lambda_1 + (1-\alpha)\lambda_2) \leq \alpha\mathcal{Z}(\lambda_1) + (1-\alpha)\mathcal{Z}(\lambda_2)$$

2. The function $f_\epsilon(x) = (e^{(\lambda+\epsilon)x} - e^{\lambda x})/\epsilon$ converges pointwise to $xe^{\lambda x}$, and $|f_\epsilon(x)| \leq e^{\lambda x}(e^{\delta|x|} - 1)/\delta \leq e^{\lambda x}(e^{\delta x} + e^{-\delta x})/\delta = h(x)$, for every $|\epsilon| \leq \delta$. For any $\lambda \in \mathcal{D}^o_{\mathcal{Z}}$, there exists a $\delta > 0$ small enough such that $\mathbb{E}(h(X_1)) \leq M(\lambda+\delta) + M(\lambda-\delta) < +\infty$. Then the result follows by the dominated convergence theorem.

□

Using the same argument one can prove that $\mathcal{Z}(\cdot) \in \mathcal{C}^\infty(\mathcal{D}^o_{\mathcal{Z}})$. Computing the second derivative we obtain

$$\mathcal{Z}''(\lambda) = \frac{\mathbb{E}(X_1^2 e^{\lambda X_1})}{M(\lambda)} - \left(\frac{\mathbb{E}(X_1 e^{\lambda X_1})}{M(\lambda)}\right)^2 \geq 0$$

Observe that $\mathcal{Z}''(0) = \text{Var}(X_1)$. To avoid the trivial deterministic case, we assume that $\text{Var}(X_1) > 0$. It follows that $\mathcal{Z}''(\lambda) > 0$ for any $\lambda \in \mathcal{D}^o_{\mathcal{Z}}$, i.e. $\mathcal{Z}(\cdot)$ is strictly convex.

We define the rate function as the Fenchel-Legendre transform of $\mathcal{Z}$

$$I(x) = \sup_{\lambda\in\mathbb{R}} \{\lambda x - \mathcal{Z}(\lambda)\} \tag{2.2.3}$$

It is immediate to see that I is convex (as supremum of linear functions), hence continuous, and that $I(x) \geq 0$. Furthermore we have that $I(m) = 0$. In fact by Jensen's inequality $M(\lambda) \geq e^{\lambda m}$ for any $\lambda \in \mathbb{R}$, so that

$$\lambda m - \mathcal{Z}(\lambda) \leq 0$$

and it is equal to 0 for $\lambda = 0$. We conclude that $I(m) = 0$.

Consequently m is a minimum of the convex positive function $I(x)$. It follows that $I(x)$ is nondecreasing for $x \geq m$ and nonincreasing for $x \leq m$.

Observe that if $x > m$ and $\lambda < 0$

$$\lambda x - \mathcal{Z}(\lambda) \leq \lambda m - \mathcal{Z}(\lambda)$$

that implies

$$I(x) = \sup_{\lambda\geq 0} \{\lambda x - \mathcal{Z}(\lambda)\} \qquad x > m \tag{2.2.4}$$

Similarly one obtains

$$I(x) = \sup_{\lambda\leq 0} \{\lambda x - \mathcal{Z}(\lambda)\} \qquad x < m \tag{2.2.5}$$

Here are other important properties of $I(\cdot)$:

Lemma 2.2.2 *$I(x) \to +\infty$ as $|x| \to \infty$, and its level sets are compact.*

Proof: If $x > m \vee 0$, for any positive $\lambda \in \mathcal{D}_{\mathcal{Z}}$,

$$\frac{I(x)}{x} \geq \lambda - \frac{\mathcal{Z}(\lambda)}{x}$$

and $\lim_{x\to+\infty} \mathcal{Z}(\lambda)/x = 0$, so we have $\lim_{x\to+\infty} I(x)/x \geq \lambda$. Consequently its level sets $\{x : I(x) \leq a\}$ are bounded, and closed by continuity of I. $\square$

We want to prove the following theorem:

Theorem 2.2.3 (Cramer) *For any set $A \subset \mathbb{R}$,*

$$-\inf_{x\in A^o} I(x) \leq \liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in A) \leq \limsup_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in A) \leq -\inf_{x\in\bar{A}} I(x)$$

were A^o is the interior of A and $\bar{A}$ is the closure of A.

2.2.1 Properties of Legendre transforms

We denote $\mathcal{D}_I = \{x \in \mathbb{R} : I(x) < \infty\}$.

Lemma 2.2.4

The function I is convex in $\mathcal{D}_I$, strictly convex in $\mathcal{D}_I^0$ and $I \in C^\infty(\mathcal{D}_I^o)$. Furthermore for any $\bar{x} \in \mathcal{D}_I^o$ there exists a unique $\bar{\lambda} \in \mathcal{D}_{\mathcal{Z}}^o$ such that

$$\bar{x} = \mathcal{Z}'(\bar{\lambda})$$

and

$$\bar{\lambda} = I'(\bar{x})$$

Furthermore $I(\bar{x}) = \bar{\lambda}\bar{x} - \mathcal{Z}(\bar{\lambda})$.

We will say that $\bar{x}$ and $\bar{\lambda}$ are in duality if the conditions of the above lemma are satisfied.

Proof: The function $F_x(\lambda) = \lambda x - \mathcal{Z}(\lambda)$ has a maximum for $\lambda = \bar{\lambda}$. This is because it is concave and $\partial_\lambda F_x(\bar{\lambda}) = 0$. It follows that $I(\bar{x}) = \bar{\lambda}\bar{x} - \mathcal{Z}(\bar{\lambda})$ and that $\mathcal{Z}(\lambda) = \sup_x \{\lambda x - I(x)\}$. By the same argument $G_\lambda(x) = \lambda x - I(x)$ is maximized by $\bar{x}$. $\square$

2.2.2 Proof of Cramer's theorem

Upper bound

Let us start with A a closed interval of the form $J_x = [x, +\infty)$ and let $x > m$. Then the exponential Chebycheff's inequality gives for any $\lambda > 0$

$$\mathbb{P}(\hat{S}_n \geq x) \leq e^{-n\lambda x}\mathbb{E}[e^{\sum_{i=1}^n \lambda X_i}] = e^{-n\lambda x} M(\lambda)^n$$

Since $\lambda > 0$ is arbitrary, we can optimize the bound and obtain for $x > m$

$$\frac{1}{n} \log \mathbb{P}(\hat{S}_n \geq x) \leq -\sup_{\lambda > 0}\{\lambda x - \mathcal{Z}(\lambda)\} = -I(x) \tag{2.2.6}$$

where we use (2.2.4) in the last equality. Similarly for $x < m$ we obtain

$$\frac{1}{n} \log \mathbb{P}(\hat{S}_n \leq x) \leq -\sup_{\lambda < 0}\{\lambda x - \mathcal{Z}(\lambda)\} = I(x) \tag{2.2.7}$$

Consider now an arbitrary closed set $C \subset \mathbb{R}$. If $m \in C$, then $\inf_{x\in C} I(x) = 0$ and the upper bound is trivial.

If $m \notin C$, let (x_1, x_2) be the largest open interval around m such that $C \cap (x_1, x_2) = \emptyset$, i.e.

$$C \subseteq (-\infty, x_1] \cup [x_2, +\infty)$$

(if $x_1 = -\infty$ then $C \subseteq [x_2, +\infty)$ and if $x_2 = +\infty$ then $C \subseteq (-\infty, x_1]$). Observe that $x_1 < m < x_2$. Consequently

$$\mathbb{P}(\hat{S}_n \in C) \leq \mathbb{P}(\hat{S}_n \geq x_2) + \mathbb{P}(\hat{S}_n \leq x_1) \leq 2\max\{\mathbb{P}(\hat{S}_n \geq x_2), \mathbb{P}(\hat{S}_n \leq x_1)\}$$

and using (2.2.6) and (2.2.7)

$$\frac{1}{n}\log \mathbb{P}(\hat{S}_n \in C) \leq -\min\{I(x_2), I(x_1)\} + \frac{1}{n}\log 2 \tag{2.2.8}$$

and from the monotonicity of $I(x)$ on $(-\infty, x_1]$ and $[x_2, +\infty)$

$$\inf_{x\in C} I(x) \geq \min\{I(x_2), I(x_1)\}$$

which concludes the upper bound.

Lower bound

Given an open set G, it is enough to prove that for any $x \in G$

$$\liminf_{n\to\infty} \frac{1}{n}\log \mathbb{P}(\hat{S}_n \in G) \geq -I(x) \ .$$

To this end, it is enough to prove that for any x and any $\delta > 0$,

$$\liminf_{n\to\infty} \frac{1}{n}\log \mathbb{P}(\hat{S}_n \in (x-\delta, x+\delta)) \geq -I(x) \ .$$

Clearly it is enough to consider x such that $I(x) < \infty$. Assume α has finite support and that $\alpha((-\infty, 0)) > 0, \alpha((0,\infty)) > 0$. Then $\mathcal{Z}$ is finite everywhere ($\mathcal{D}_{\mathcal{Z}} = \mathcal{D}^o_{\mathcal{Z}} = \mathbb{R}$) and there exists a unique $\lambda_0 \in \mathcal{D}^o_{\mathcal{Z}}$ such that

$$I(x) = \lambda_0 x - \mathcal{Z}(\lambda_0) \qquad \text{and} \qquad x = \mathcal{Z}'(\lambda_0)$$

Assuming $x \geq m$, we have that $\lambda_0 \geq 0$.

Let us define the probability law on $\mathbb{R}$

$$\alpha_{\lambda_0}(dy) = \frac{e^{\lambda_0 y}}{M(\lambda_0)}\alpha(dy)$$

Notice that

$$\int y\ \alpha_{\lambda_0}(dy) = \mathcal{Z}'(\lambda_0) = x$$

Noting $A_{n,\delta} = \{(x_1, \ldots, x_n) : (x_1 + \cdots + x_n)/n \in (x - \delta, x + \delta)\} \subset \mathbb{R}^n$, then for $\delta_1 < \delta$

$$\begin{aligned}
\mathbb{P}(\hat{S}_n \in (x-\delta, x+\delta)) &\geq \int_{A_{n,\delta_1}} \alpha(dx_1)\ldots\alpha(dx_n) \\
= M(\lambda_0)^n &\int_{A_{n,\delta_1}} e^{-\lambda_0(x_1+\cdots+x_n)}\alpha_{\lambda_0}(dx_1)\ldots\alpha_{\lambda_0}(dx_n) \\
\geq M(\lambda_0)^n e^{-n\lambda_0(x+\delta_1)} &\int_{A_{n,\delta_1}} \alpha_{\lambda_0}(dx_1)\ldots\alpha_{\lambda_0}(dx_n)
\end{aligned}$$

By the law of large numbers, for any $\delta_1 > 0$

$$\int_{A_{n,\delta_1}} \alpha_{\lambda_0}(dx_1)\ldots\alpha_{\lambda_0}(dx_n) \underset{n\to\infty}{\longrightarrow} 1$$

so that

$$\liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in (x-\delta, x+\delta)) \geq -\left[\lambda_0(x+\delta_1) - \mathcal{Z}(\lambda_0)\right] = -I(x) - \lambda_0\delta_1$$

Since $\delta_1 < \delta$ is arbitrary, we can let $\delta_1 \to 0$ and it gives the result. If $x < m$, we have $\lambda_0 < 0$, and in the steps of the above we will have $x - \delta_1$ instead of $x + \delta_1$.

Assume now α is of unbounded support with $\alpha((-\infty, x)) > 0, \alpha((x, \infty)) > 0$. Let $A_0 > 0$ be such that $\alpha([-A_0, x)) > 0, \alpha((x, A_0]) > 0$. For any $A \geq A_0$ let β be the law of X_1 conditioned on $\{|X_1| \leq A\}$, and β_n the law of $\hat{S}_n$ conditioned on $\{|X_i| \leq A,\ i = 1, \ldots, n\}$. Then, for all $n \geq 1$ and every $\delta > 0$,

$$\alpha_n((x-\delta, x+\delta)) = \beta_n((x-\delta, x+\delta))\,\{\alpha([-A, A])\}^n$$

The preceding result applies for β_n. Note

$$\mathcal{Z}^A(\lambda) = \log \int_{-A}^{A} e^{\lambda y}\alpha(dy),$$

and observe that the logarithmic generating function of β is given by

$$\mathcal{Z}^A(\lambda) - \log\alpha([-A, A]) \ \geq\ \mathcal{Z}^A(\lambda)$$

It follows that

$$\liminf_{n\to\infty} \frac{1}{n} \log \alpha_n((x-\delta, x+\delta)) \geq \inf_{\lambda\in\mathbb{R}} \left\{\mathcal{Z}^A(\lambda) - \lambda x\right\} \tag{2.2.9}$$

Let us define

$$I^*(x) = \limsup_{A\to\infty} \left[\sup_{\lambda\in\mathbb{R}} \left\{ \lambda x - \mathcal{Z}^A(\lambda) \right\} \right]$$

then we have

$$\liminf_{n\to\infty} \frac{1}{n} \log \alpha_n((x-\delta, x+\delta)) \geq -I^*(x) \tag{2.2.10}$$

Observe that $\mathcal{Z}^A(\cdot)$ is nondecreasing in A, $\mathcal{Z}^A(0) \leq \mathcal{Z}(0) = 0$, and thus $-I^*(x) \leq 0$. Moreover the assumption $\alpha([-A_0, x)) > 0, \alpha((x, A_0]) > 0$ implies

$$\lambda x - \mathcal{Z}^A(\lambda) \geq -\inf \left\{ \log \alpha[-A_0, x) \, , \, \log \alpha(x, A_0] \right\}$$

Therefore we have $-I^*(x) > -\infty$. The level sets $\{\lambda; \mathcal{Z}^A(\lambda) - \lambda x \leq -I^*(x)\}$ are non-empty, compact sets that are nested with respect to A. Then it exists λ_0 in their intersection and $-I(x) \leq \mathcal{Z}(\lambda_0) - \lambda_0 x = \lim_{A\to\infty} \mathcal{Z}^A(\lambda_0) - \lambda_0 x \leq -I^*(x)$. By (2.2.10) we get

$$\liminf_{n\to\infty} \frac{1}{n} \log \alpha_n((x-\delta, x+\delta)) \geq -I(x)$$

The proof for an arbitrary probability law α is completed by observing that if either $\alpha((-\infty, x))$ or $\alpha((x, \infty)) = 0$ then $\mathcal{Z}(\cdot)$ is a monotone function with $\inf_{\lambda\in\mathbb{R}}\{\mathcal{Z}(\lambda) - \lambda x\} = \log \alpha(\{x\})$. Then we have

$$\alpha_n((x-\delta, x+\delta)) \geq \alpha_n(\{x\}) = \alpha(\{x\})^n$$

and

$$\liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in (x-\delta, x+\delta)) \geq -I(x)$$

□

Remark 2.2.5 *Notice that the proof contains the non-asymptotic bound* (2.2.8)*, i.e.*

$$\forall n \geq 1, \quad \mathbb{P}(\hat{S}_n \in C) \leq 2e^{-n \inf_{x\in C} I(x)} \tag{2.2.11}$$

also called Chernoff's bound.

Remark 2.2.6 *The lower bound was obtained by using the change of variable in conjunction with the law of large numbers for the new probabilities. One can get better bound by using the central limit theorem, and obtain the following corollary*

Corollary 2.2.7 *For any $x > m$,*

$$\begin{aligned} \lim_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \geq x) &= -I(x) \qquad \text{if } x > m \\ \lim_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \leq x) &= -I(x) \qquad \text{if } x < m \end{aligned} \tag{2.2.12}$$

Proof: By the central limit theorem

$$\int_{\{x_1+\cdots+x_n/n\in[x,x+\delta_1)\}} \alpha_{\lambda_0}(dx_1)\ldots\alpha_{\lambda_0}(dx_n) \underset{n\to\infty}{\longrightarrow} \frac{1}{2}$$

So in the proof of the lower bound one can substitute $(x-\delta, x+\delta)$ with $[x, x+\delta)$. Since $\mathbb{P}(\hat{S}_n \geq x) \geq \mathbb{P}(\hat{S}_n \in [x, x+\delta))$ one obtains

$$\liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \geq x) \geq -I(x)$$

The upper bound follows from the one in theorem 2.2.3.

Examples in $\mathbb{R}$

1. Let α be the gaussian distribution

$$\frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-m)^2/2\sigma^2}\, dx$$

   then $I(x) = (x-m)^2/2\sigma^2$. In this case one can compute it directly, since $\hat{S}_n - nm$ has law $\mathcal{N}(0, \sigma^2/n)$.

2. $\alpha = \frac{1}{2}(\delta_0 + \delta_1)$ (Bernoulli). Then $M(\lambda) = \frac{1}{2}(1+e^\lambda)$ and

$$I(x) = x\log x + (1-x)\log(1-x) + \log 2 \qquad \text{if } x \in [0,1]$$

   and $I(x) = +\infty$ otherwise.

3. For the exponential law $\alpha(dx) = \beta e^{-\beta x} 1_{x\geq 0}\, dx$, we have $M(\lambda) = \beta/(\beta-\lambda)$ for $-\infty < \lambda < \beta$, otherwise $M(\lambda) = +\infty$. Then

$$I(x) = \beta x - 1 - \log(\beta x) \qquad \text{if } x > 0$$

   and $I(x) = +\infty$ if $x \leq 0$.

4. If ξ in a random variable with law $\mathcal{N}(0, 1/\beta)$, then ξ^2 has law $\chi^2(1)$, i.e. a gamma law $\Gamma(1/2, \beta/2)$, which has density

$$\frac{\beta^{1/2}}{\sqrt{2}\Gamma(1/2)} x^{-1/2} e^{-\beta x}$$

Its moment generating function is $M(\lambda) = (\beta/(\beta - 2\lambda))^{1/2}$ if $\lambda < \beta/2$, otherwise equal to $+\infty$. The rate function results

$$I(x) = \frac{1}{2}\{\beta x - \log(\beta x) - 1\} \qquad \text{if } x > 0$$

and $+\infty$ if $x < 0$.

2.3 Cramér's Theorem in $\mathbb{R}^d$

Let $\{\mathbf{X}_n\}$ be a sequence of i.i.d. random variables in $\mathbb{R}^d$, and denote $\alpha(d\mathbf{x})$ the common law. We define as before, for $\mathbf{u} \in \mathbb{R}^d$, the moment generating function and its logarithm

$$M(\mathbf{u}) = \int_{\mathbb{R}^d} e^{\mathbf{u}\cdot\mathbf{x}}\, \alpha(d\mathbf{x}), \qquad \mathcal{Z}(\mathbf{u}) = \log M(\mathbf{u}) \tag{2.3.1}$$

and we denote $\mathcal{D}_{\mathcal{Z}} = \{\mathbf{u} \in \mathbb{R}^d : \mathcal{Z}(\mathbf{u}) < +\infty\}$. We assume that $0 \in \mathcal{D}^o_{\mathcal{Z}}$. Then $M(\mathbf{u})$ is smooth in this open set and $\nabla M(0) = \mathbf{m} = \mathbb{E}(\mathbf{X}_1)$.

The rate function is the Legendre-Fenchel transform of $\mathcal{Z}$:

$$I(\mathbf{x}) = \sup_{\mathbf{u}\in\mathbb{R}^d} \{\mathbf{u}\cdot\mathbf{x} - \mathcal{Z}(\mathbf{u})\} \tag{2.3.2}$$

As in the one dimensional case, it follows immediately from the definition that I is non negative, convex, lower semicontinuous and $I(\mathbf{m}) = 0$. Denoting $\mathcal{D}_I = \{\mathbf{x} : I(\mathbf{x}) < +\infty\}$ we have similar properties as in the one dimensional case:

Lemma 2.3.1 *$I(\mathbf{x}) \in \mathcal{C}^\infty(\mathcal{D}_I{}^o)$, and $\mathbf{m} \in (\mathcal{D}_I{}^o)$. There exists a diffeomorphism between $\mathcal{D}_I{}^o$ and $\mathcal{D}^o_\lambda$ defined by*

$$\mathbf{u}^* = (\nabla\mathcal{Z})(\mathbf{u}), \quad \mathbf{u} = (\nabla I)(\mathbf{u}^*) \tag{2.3.3}$$

and

$$(\nabla^2\mathcal{Z})(\mathbf{u}) = \left[\nabla^2 I)(\mathbf{u}^*)\right]^{-1} \tag{2.3.4}$$

Theorem 2.3.2 *For any Borel set $A \subset \mathbb{R}^d$,*

$$-\inf_{\mathbf{x}\in A^o} I(\mathbf{x}) \leq \liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in A) \leq \limsup_{n\to\infty} \frac{1}{n} \log \mathbb{P}(\hat{S}_n \in A) \leq -\inf_{\mathbf{x}\in\bar{A}} I(\mathbf{x})$$

were A^o is the interior of A and $\bar{A}$ is the closure of A.

Proof:

The lower bound is proven in the same way as in $d = 1$. Consider $\mathbf{u}^*$ such that $I(\mathbf{u}^*) < +\infty$. To simplify we assume there exists a unique $\mathbf{u} \in \mathcal{D}_I^o$ such that

$$I(\mathbf{u}^*) = \mathbf{u}^* \cdot \mathbf{u} - \mathcal{Z}(\mathbf{u}) \qquad \mathbf{u} = (\nabla I)(\mathbf{u}^*)$$

Then we consider the new probability law on $\mathbb{R}^d$, absolutely continuous with respect to α, defined by

$$\alpha_{\mathbf{u}}(d\mathbf{x}) = e^{\mathbf{u}\cdot\mathbf{x}-\mathcal{Z}(\mathbf{u})}\, \alpha(d\mathbf{x})$$

Observe that

$$\int \mathbf{x}\alpha_{\mathbf{u}}(d\mathbf{x}) \;=\; \mathbf{u}^*$$

Noting $A_{n,\delta} = \{(\mathbf{x}_1, \ldots, \mathbf{x}_n) : |(\mathbf{x}_1 + \cdots + \mathbf{x}_n)/n - \mathbf{u}^*| \leq \delta\} \subset \mathbb{R}^n$, then for any $\delta_1 < \delta$

$$\begin{aligned}
\mathbb{P}(|\hat{\mathbf{S}}_n - \mathbf{u}^*| < \delta) &\geq \int_{A_{n,\delta_1}} \alpha(d\mathbf{x}_1) \ldots \alpha(d\mathbf{x}_n) \\
&= M(\mathbf{u})^n \int_{A_{n,\delta_1}} e^{-\mathbf{u}\cdot(\mathbf{x}_1+\cdots+\mathbf{x}_n)} \alpha_{\mathbf{u}}(d\mathbf{x}_1) \ldots \alpha_{\mathbf{u}}(d\mathbf{x}_n) \\
&= M(\mathbf{u})^n e^{-n\mathbf{u}\cdot\mathbf{u}^*} \int_{A_{n,\delta_1}} e^{-\mathbf{u}\cdot[(\mathbf{x}_1+\cdots+\mathbf{x}_n)-n\mathbf{u}^*]} \alpha_{\mathbf{u}}(d\mathbf{x}_1) \ldots \alpha_{\mathbf{u}}(d\mathbf{x}_n) \\
&\geq e^{-nI(\mathbf{u}^*)} e^{-n|\mathbf{u}|\delta_1} \int_{A_{n,\delta_1}} \alpha_{\mathbf{u}}(d\mathbf{x}_1) \ldots \alpha_{\mathbf{u}}(d\mathbf{x}_n)
\end{aligned}$$

The law of large numbers now says that

$$\lim_{n\to\infty} \int_{A_{n,\delta_1}} \alpha_{\mathbf{u}}(d\mathbf{x}_1) \ldots \alpha_{\mathbf{u}}(d\mathbf{x}_n) = 1$$

and we obtain

$$\liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(|\hat{\mathbf{S}}_n - \mathbf{u}^*| < \delta) \geq -I(\mathbf{u}^*) - |\mathbf{u}|\delta_1$$

and letting $\delta_1 \to 0$ we conclude that for any $\delta > 0$ we have the lower bound

$$\liminf_{n\to\infty} \frac{1}{n} \log \mathbb{P}(|\hat{\mathbf{S}}_n - \mathbf{u}^*| < \delta) \geq -I(\mathbf{u}^*)$$

The upper bound requires a little more work. Convexity plays a role here.

Let C any Borel set in $\mathbb{R}^d$. Then the exponential Chebicheff inequality implies for any $\mathbf{u} \in \mathbb{R}^d$

$$\mathbb{P}\left(\hat{\mathbf{S}}_n \in C\right) \leq \exp\left[-n \inf_{\mathbf{x}\in C} \mathbf{u}\cdot\mathbf{x}\right] \mathbb{E}\left(e^{n\mathbf{u}\cdot\hat{\mathbf{S}}_n}\right) = \exp\left[-n \inf_{\mathbf{x}\in C} \mathbf{u}\cdot\mathbf{x}\right] M(\mathbf{u})^n$$

and optimizing in $\mathbf{u} \in \mathbb{R}^d$ we obtain

$$\frac{1}{n}\log\mathbb{P}\left(\hat{\mathbf{S}}_n \in C\right) \leq -\sup_{\mathbf{u}\in\mathbb{R}^d}\inf_{\mathbf{x}\in C}\left[\mathbf{u}\cdot\mathbf{x} - \mathcal{Z}(\mathbf{u})\right] \tag{2.3.5}$$

So to conclude we need to exchange "$\sup_{\mathbf{u}\in\mathbb{R}^d}$" with "$\inf_{\mathbf{x}\in C}$". This is immediate if C is a convex set by the following lemma (c.f. [3], chapter 6):

Lemma 2.3.3 *Let $g(\mathbf{u},\mathbf{x})$ be convex and lower semicontinuous in $\mathbf{x}$, concave and uppersemicontinuous in $\mathbf{u}$, then if C is compact and convex*

$$\inf_{\mathbf{x}\in C}\sup_{\mathbf{u}\in\mathbb{R}^d} g(\mathbf{u},\mathbf{x}) = \sup_{\mathbf{u}\in\mathbb{R}^d}\inf_{\mathbf{x}\in C} g(\mathbf{u},\mathbf{x}) \tag{2.3.6}$$

Consider now any compact set $K \subset \mathbb{R}^d$,there exists $l > 0$ such that $\inf_{\mathbf{x}\in K} I(\mathbf{x}) = l$. By the ower semicontinuity of $I(\cdot)$, for a fixed $\epsilon > 0$ and any $\mathbf{x}' \in K$, there exists a closed ball $C(\mathbf{x}')$ such that

$$I(\mathbf{x}) \geq l - \epsilon \qquad \forall \mathbf{x} \in C(\mathbf{x}')$$

Since K is compact, there exists a finite subcover $C(\mathbf{x}'_1), \ldots, C(\mathbf{x}'_N)$ extracted from these closed ball. Then

$$\begin{aligned}\mathbb{P}\left(\hat{\mathbf{S}}_n \in K\right) &\leq \sum_{j=1}^{N}\mathbb{P}\left(\hat{\mathbf{S}}_n \in C(\mathbf{x}'_j)\right) \leq N\max_{1\leq j\leq N}\mathbb{P}\left(\hat{\mathbf{S}}_n \in C(\mathbf{x}'_j)\right)\\ &\leq N\max_{1\leq j\leq N}\exp\left(-n\inf_{C(\mathbf{x}'_j)} I\right) \leq Ne^{-n(l-\epsilon)}\end{aligned}$$

and

$$\limsup_{n\to\infty}\frac{1}{n}\log\mathbb{P}\left(\hat{\mathbf{S}}_n \in K\right) \leq -(l-\epsilon)$$

Since ϵ is arbitrary, this proves the upper bound for compact sets.

To extend this bound from compact to closed sets, we need to prove the *exponential tightness* of the distribution of $\hat{\mathbf{S}}_n$, i.e.

$$\lim_{\rho\to\infty}\lim_{n\to\infty}\frac{1}{n}\log\mathbb{P}\left(\hat{\mathbf{S}}_n \notin H_\rho\right) = -\infty \tag{2.3.7}$$

where $H_\rho = [-\rho, \rho]^d$ is the centered hypercube of length 2ρ. To prove this observe that, denoting $\hat{S}_n^{(j)}$ is the average of $X_1^{(j)}, \ldots, X_n^{(j)}$, by applying the results obtained in the one-dimensional case, we have

$$\mathbb{P}\left(\hat{\mathbf{S}}_n \notin H_\rho\right) \leq \sum_{j=1}^{d} \mathbb{P}\left(\hat{S}_n^{(j)} \notin (-\rho, \rho)\right) \leq d \max_{j=1,\ldots,d} \exp\left(-n \min\{I^j(\rho), I^j(-\rho)\}\right)$$

where I^j is the rate function for the $j-$marginal distribution of the law α. Then (2.3.7) follows by applying lemma 2.2.2.

□

2.4 Generalities on Large Deviations

Let X a complete separable metric space and P_n a family of probability distributions on X. In the previous sections $X = \mathbb{R}^d$ and P_n the distribution of $\hat{S}_n$. We says that $\{P_n\}$ satisfies a large deviation principle with good rate function $I(\cdot)$ if there exists a function $I : X \to [0, \infty]$ such that:

1. $I(\cdot)$ is lower semicontinuous.
2. For each $\ell < \infty$ the set $\{x : I(x) \leq \ell\}$ is compact in X.
3. For each closed set $C \subset X$
$$\limsup_{n\to\infty} \frac{1}{n} \log P_n(C) \leq -\inf_{x \in C} I(x).$$
4. For each open set $G \subset X$
$$\liminf_{n\to\infty} \frac{1}{n} \log P_n(G) \geq -\inf_{x \in G} I(x).$$

Here the adjective *good* refers to properties 1 and 2. The next lemma does not require the rate function I to be good.

Theorem 2.4.1 ***Varadhan's Lemma.*** *Let P_n satisfy the large deviation principle with rate function I. Then for any bounded continuous function $F(x)$ on X*

$$\lim_{n\to\infty} \frac{1}{n} \log \int e^{nF(x)} dP_n(x) = \sup_{x \in X}\{F(x) - I(x)\}.$$

Proof.

Upper bound. For any given $\delta > 0$, since F is bounded and continuous, we can find a finite number of closed sets covering X such that the oscillation of $F(\cdot)$ on each of these closed sets is less or equal δ. Then

$$\int e^{nF(x)} dP_n(x) \le \sum_{j=1}^{m} \int_{C_j} e^{nF(x)} dP_n(x) \le \sum_{j=1}^{m} e^{nF_j+\delta} P_n(C_j)$$

where $F_j = \inf_{C_j} F(x)$. It follows

$$\begin{aligned}\limsup_{n\to\infty} \frac{1}{n} \log \int e^{nF(x)} dP_n(x) &\le \sup_{1\le j\le m} [F_j + \delta - \inf_{C_j} I(x)] \\ &\le \sup_{1\le j\le m} \sup_{C_j} [F(x) - I(x)] + \delta \\ &= \sup_{x\in X} [F(x) - I(x)] + \delta\end{aligned}$$

Since δ is arbitrary, we can let it go to 0.

Lower bound. By definition of a supremum for any $\delta > 0$ we can find $y \in X$ such that $F(y) - I(y) \ge \sup_x [F(x) - I(x)] - \delta/2$. Since F is continuous we can find an open neighborhood U of y such that $F(x) \ge F(y) - \delta/2$ for any $x \in U$. Then we obtain

$$\liminf_{n\to\infty} \frac{1}{n} \log \int e^{nF(x)} dP_n(x) \ge \liminf_{n\to\infty} \frac{1}{n} \log \int_U e^{nF(x)} dP_n(x)$$

$$\ge F(y) - \frac{\delta}{2} - \inf_{x\in U} I(x) \ge F(y) - I(y) - \frac{\delta}{2} \ge \sup_x [F(x) - I(x)] - \delta$$

and we conclude from the arbitrariness of δ. □

Theorem 2.4.2 ***Contraction Principle.*** *Let P_n satisfy the large deviation principle with rate function I, and $\pi : X \to Y$ a continuous mapping from X to another complete separable metric space Y. Then $\tilde{P}_n = P_n \pi^{-1}$ satisfies a large deviation principle with rate function*

$$\begin{aligned}\tilde{I}(y) &= \inf_{x:\pi(x)=y} I(x), \\ \tilde{I}(y) &= +\infty \qquad \textit{if } \{x : \pi(x) = y\} = \emptyset\end{aligned}$$

Proof. Since π is continuous, given any closed set $\tilde{C} \subset Y$, the subset $C = \pi^{-1}(\tilde{C})$ is closed in X. Then

$$\limsup_{n\to\infty} \frac{1}{n} \log \tilde{P}_n(\tilde{C}) = \limsup_{n\to\infty} \frac{1}{n} \log P_n(C) \le - \inf_{x\in C} I(x) = - \inf_{y\in \tilde{C}} \inf_{x:\pi(x)=y} I(x).$$

and similarly for the lower bound. □

2.5 Large deviations for densities

We deal first with the one-dimensional case. If the distribution of $\hat{S}_n$ on $\mathbb{R}$ has a density that we denote by $f_n(x)$, from Cramers theorem we have the intuition that $f_n(x) \sim e^{-nI(x)}$ for large n. We will prove this under some condition on the probability $\alpha(dx)$. It is interesting to notice that we will not use Cramer's theorem in the proof, but the following *local central limit theorem.*

Theorem 2.5.1 ***Local central limit theorem.*** *Let $\phi(k)$ the characteristic function of a centered probability measure $\alpha(dx)$ with finite variance σ^2, and assume that $|\phi(k)| < 1$ if $k \neq 0$ and that there exists an integer $r \geq 1$ such that $|\phi|^r$ is integrable. Let $\tilde{g}_n(x)$ the probability density of $(X_1 + \cdots + X_n)/\sqrt{n}$, where X_j are i.i.d. with common law α. Then*

$$\lim_{n\to\infty} \tilde{g}_n(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}.$$

Proof. The characteristic function of α is defined by

$$\phi(k) = \int e^{ixk}\alpha(dx) \tag{2.5.1}$$

The characteristic function of the distribution of $X_1 + \cdots + X_r$ is $\phi^r(k)$ that is integrable. It follows that the probability density $\tilde{g}_n(x)$ exists for any $n \geq r$ (cf. [**?**], theorem XV.3.3). Then

$$\tilde{g}_n(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-ixk}\left[\phi\left(\frac{k}{\sqrt{n}}\right)\right]^n dk$$

and therefore

$$\left|\tilde{g}_n(x) - \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/2\sigma^2}\right| \leq \frac{1}{2\pi}\int_{-\infty}^{+\infty} \left|\phi\left(\frac{k}{\sqrt{n}}\right)^n - e^{-k^2\sigma^2/2}\right| dk$$

Given $a > 0$, we split the integral in three parts.

1. Uniformly in $k \in [-a, a]$,

$$\phi\left(\frac{k}{\sqrt{n}}\right)^n = \left(1 - \frac{k^2\sigma^2}{2n} + o\left(\frac{1}{n}\right)\right)^n \underset{n\to\infty}{\longrightarrow} e^{-k^2\sigma^2/2}$$

so that

$$\int_{-a}^{+a} \left|\phi\left(\frac{k}{\sqrt{n}}\right)^n - e^{-k^2\sigma^2/2}\right| dk \to 0$$

2. Observe that it is possible to choose $\delta > 0$ such that
$$|\phi(k)| \leq e^{-k^2\sigma^2/4} \qquad \text{if} \quad |k| \leq \delta.$$
Then for the interval $|k| \in (a, \delta\sqrt{n})$, we can estimate as
$$\int_a^{\delta\sqrt{n}} \left|\phi\left(\frac{k}{\sqrt{n}}\right)^n - e^{-k^2\sigma^2/2}\right| dk \leq \int_a^{\delta\sqrt{n}} 2e^{-k^2\sigma^2/4} dk \leq \int_a^{+\infty} 2e^{-k^2\sigma^2/4} dk$$
that converge to 0 as $a \to \infty$.

3. It remains to estimate the contribution from the interval $(\delta\sqrt{n}, +\infty)$. Since we assumed that $|\phi(k)| < 1$ for $k \neq 0$, and since $|\phi|^k$ is integrable, we have $\phi(k) \to 0$ as $k \to \infty$. Consequently we must have $\sup_{|k|\geq\delta} |\phi(k)| = \eta < 1$, and we can estimate
$$\begin{aligned}\int_{\delta\sqrt{n}}^{+\infty} \left|\phi\left(\frac{k}{\sqrt{n}}\right)^n - e^{-k^2\sigma^2/2}\right| dk &\leq \eta^{n-r} \int_{-\infty}^{+\infty} \left|\phi\left(\frac{k}{\sqrt{n}}\right)\right|^r dk + \int_{\delta\sqrt{n}}^{+\infty} e^{-k^2\sigma^2/2} dk \\ &= \eta^{n-r}\sqrt{n} \int_{-\infty}^{+\infty} |\phi(k)|^r dk + \int_{\delta\sqrt{n}}^{+\infty} e^{-k^2\sigma^2/2} dk\end{aligned}$$
that converges to 0 as $n \to \infty$.

□

Distributions such that their characteristic function $|\phi(k)| < 1$ for $k \neq 0$ are called *non-lattice* ([2], chapter 2). It does not imply they have density.

We assume now that the measure $\alpha(dx)$ satisfies all the assumptions made in section 2.2, and furthermore its characteristic function satisfies conditions of the local central limit theorem 2.5.1. Then, for $n \geq r$, the distribution of $\hat{S}_n$ on $\mathbb{R}$ has a density that we denote by $f_n(x)$.

Theorem 2.5.2 *For any $y \in \mathcal{D}_I^o$ we have*
$$\lim_{n\to\infty} \frac{1}{n} \log f_n(y) = -I(y) \ . \tag{2.5.2}$$

Proof.

Let $\tau_y\alpha$ the translation of the measure α by y. Assume that $m = \int x\alpha(dx) = 0$, otherwise just recenter it and consider $\tau_m\alpha$.

Let $y \in \mathcal{D}_I{}^o$. Then by lemma 2.2.4 there exists a unique $\lambda \in \mathcal{D}_\mathcal{Z}{}^o$ such that $y = \mathcal{Z}'(\lambda)$, $\lambda = I'(y)$, and $I(y) = \lambda y - \mathcal{Z}(\lambda)$. Define
$$\tilde{\alpha}(y, dx) = \frac{1}{M(\lambda)} e^{(x+y)\lambda} \tau_y\alpha(dx)$$

Observe that this is a probability distribution with 0 average. In fact

$$\int \tilde{\alpha}(y, dx) = \frac{1}{M(\lambda)} \int e^{z\lambda} \alpha(dz) = 1$$

and

$$\int x\tilde{\alpha}(y, dx) = -y + \frac{1}{M(\lambda)} \int z e^{z\lambda} \alpha(dz) = -y + \mathcal{Z}'(\lambda) = 0$$

So we treat here y as a parameter. Let $X_1^y, \dots, X_n^y$ i.i.d. random variables with law given by $\tilde{\alpha}(y, dx)$.

For $n \geq r$ it exists the density for the distribution of $(X_1^y + \cdots + X_n^y)/n$ that we denote by $f_n(x, y)$, and it is equal to

$$f_n(x, y) = \frac{e^{n(x+y)\lambda}}{M(\lambda)^n} f_n(x + y) = e^{n(I(y)+\lambda x)} f_n(x + y)$$

To prove this formula, compute, for a given bounded measurable function $G(\cdot)$:

$$\begin{aligned} \mathbb{E}\left(G((X_1^y + \cdots + X_n^y)/n)\right) &= \int_{\mathbb{R}^n} G(\hat{s}_n) e^{n(I(y)+\lambda \hat{s}_n)} \tau_y \alpha(dx_1) \dots \tau_y \alpha(dx_n) \\ &= \int_{\mathbb{R}} G(\hat{s}) e^{n(I(y)+\lambda \hat{s})} f_n(\hat{s} + y) d\hat{s} \end{aligned} \tag{2.5.3}$$

It follows that

$$f_n(y) = e^{-nI(y)} f_n(0, y)$$

To conclude we only need to prove that $(\log f_n(0, y))/n \to 0$ as $n \to \infty$.

Let $\tilde{f}_n(x, y)$ the density of $(X_1^y + \cdots + X_n^y)/\sqrt{n}$. Then $f_n(x, y) = \sqrt{n}\tilde{f}_n(\sqrt{n}x, y)$. By the local central limit theorem 2.5.1, the result follows immediately. □

For $y \in \mathbb{R}$ define $\nu_y^{(n)}(dx_1, \dots, dx_n)$ the conditional distribution of $(X_1, \dots, X_n)$ on the hyperplane $x_1 + \cdots + x_n = ny$. This is defined as the probability measure on $\mathbb{R}^{n-1}$ satisfying the relation

$$\mathbb{E}\left(G(\hat{S}_n) H(X_1, \dots, X_n)\right) = \int_{\mathbb{R}} dy f_n(y) G(y) \int H(x_1, \dots, x_n) \nu_y^{(n)}(dx_1, \dots, dx_n)$$

Lemma 2.5.3 *Let F be a bounded continuous function on $\mathbb{R}$ and $y \in \mathcal{D}_I^o$, $\lambda = I'(y)$. For every $\theta \in \mathbb{R}$, the limit*

$$\lim_{n\to\infty} \frac{1}{n} \log \int e^{\theta(F(x_1)+\dots+F(x_n))} \nu_y^{(n)}(dx_1, \dots, dx_n) = G(y, \theta) \tag{2.5.4}$$

exists and G is differentiable at $\theta = 0$ with

$$\frac{\partial G(y, \theta)}{\partial \theta}\Big|_{\theta=0} = \int F(x) \alpha_\lambda(dx). \tag{2.5.5}$$

Proof Denote by $H_n(y,\theta)$ the function

$$\int e^{\theta(F(x_1)+....+F(x_n))}\nu_y^{(n)}(dx_1,\dots,dx_n) = \frac{H_n(y,\theta)}{f_n(y)} \tag{2.5.6}$$

which, by (2.5.3), can be formally written as

$$H_n(y,\theta) = \int_{x_1+\cdots+x_n=ny} e^{\theta(F(x_1)+....+F(x_n))}\alpha(dx_1)\dots\alpha(dx_n).$$

Let us denote

$$a(\theta) = \int e^{\theta F(x)}\alpha(dx), \qquad M(\lambda,\theta) = \frac{1}{a(\theta)}\int e^{\lambda x+\theta F(x)}\alpha(dx)$$

Then we can compute the Cramér rate function for the law $a(\theta)^{-1}e^{\theta F(x)}\alpha(dx)$, and this is given by

$$I_\theta(y) = I(y,\theta) = \sup_{\bar\lambda}\left\{\bar\lambda y - \log M(\bar\lambda,\theta)\right\}$$

Observe that $\mathcal{D}_{I_\theta} = \mathcal{D}_I$ because F is bounded. If $(Y_1,\dots,Y_n)$ are i.i.d. distributed by $a(\theta)^{-1}e^{\theta F(x)}\alpha(dx)$, then the density of the distribution of $(Y_1+\cdots+Y_n)/n$ is given by $a(\theta)^{-n}H_n(y,\theta)$. Then by applying 2.5.2 to this law we obtain

$$\lim_{n\to\infty}\frac{1}{n}\log H_n(y,\theta) = -I(y,\theta)+\log a(\theta).$$

Consequently we have, applying again 2.5.2

$$\begin{aligned}\lim_{n\to\infty}\frac{1}{n}\log\int e^{\theta(F(x_1)+....+F(x_n))}\nu_y^{(n)}(dx_1,\dots,dx_n) &= \lim_{n\to\infty}\frac{1}{n}\log H_n(y,\theta) - \lim_{n\to\infty}\frac{1}{n}\log f_n(y)\\ &= \log a(\theta) - I(y,\theta) + I(y) \equiv G(y,\theta).\end{aligned}$$

Differentiating $G(y,\theta)$ we have

$$\frac{\partial G(y,\theta)}{\partial\theta} = \frac{a'(\theta)}{a(\theta)} - \frac{\partial I(y,\theta)}{\partial\theta}$$

In order to compute this last expression let us set $\lambda^*(y,\theta) = \partial_y I(y,\theta)$. Existence of $\lambda^*(y,\theta)$ is provided by the assumption $y\in\mathcal{D}_I^o$ and the equality between the sets $\mathcal{D}_I$ and $\mathcal{D}_{I_\theta}$. We have

$$I(y,\theta) = \lambda^* y - \log M(\lambda^*,\theta).$$

Then, since $\partial_\lambda \log M(\lambda^*,\theta) = y$, we get

$$\begin{aligned}\partial_\theta I(y,\theta) &= y\partial_\theta\lambda^* - M^{-1}\left(\partial_\theta M + \partial_\lambda M\partial_\theta\lambda^*\right) = -\partial_\theta\log M(\lambda^*,\theta)\\ &= \partial_\theta\log a(\theta) - M^{-1}\partial_\theta\int e^{\lambda x+\theta F(x)}\alpha(dx) = \frac{a'(\theta)}{a(\theta)} - \int F(x)e^{\lambda^* x+\theta F(x)-\log M(\lambda^*,\theta)}\alpha(dx)\end{aligned}$$

So we have

$$\partial_\theta G(y,\theta) = \int F(x) e^{\lambda^* x + \theta F(x) - \log M(\lambda^*,\theta)} \alpha(dx)$$

and sending $\theta \to 0$ we obtain

$$\partial_\theta G(y,0) = \int F(x) e^{\lambda^*(y,0)x - \log M(\lambda^*(y,0),0)} \alpha(dx) = \int F(x)\alpha_\lambda(dx)$$

□

Theorem 2.5.4 *For any $y \in \mathcal{D}_I^o$, and any $\epsilon > 0$*

$$\lim_{n\to\infty} \nu_y^{(n)} \left(\left| \frac{1}{n}\sum_{j=1}^n F(X_j) - \int F(x)\alpha_\lambda(dx) \right| \geq \epsilon \right) = 0 \qquad (2.5.7)$$

Proof. Without loosing any generality, let us assume that $\int F(x)\alpha_\lambda(dx) = 0$. Consequently $G(\theta, y) = O(\theta^2)$. Then for any $\theta > 0$

$$\begin{aligned}
\nu_y^{(n)} \left(\left| \frac{1}{n}\sum_{j=1}^n F(X_j) \right| \geq \epsilon \right) &\leq e^{-n\theta\epsilon} \int e^{\theta |\sum_{j=1}^n F(x_j)|} \nu_y^{(n)}(dx_1,\dots,dx_n) \\
&\leq e^{-n\theta\epsilon} \int e^{\theta \sum_{j=1}^n F(x_j)} \nu_y^{(n)}(dx_1,\dots,dx_n) \\
&+ e^{-n\theta\epsilon} \int e^{-\theta \sum_{j=1}^n F(x_j)} \nu_y^{(n)}(dx_1,\dots,dx_n)
\end{aligned}$$

and by (2.5.4)

$$\lim_{n\to\infty} \frac{1}{n} \log \nu_y^{(n)} \left(\left| \frac{1}{n}\sum_{j=1}^n F(x_j) \right| \geq \epsilon \right) \leq -\theta\epsilon + \max\{G(\theta,y), G(-\theta,y)\}$$

Optimizing the above bound in θ one obtains

$$\lim_{n\to\infty} \frac{1}{n} \log \nu_y^{(n)} \left(\left| \frac{1}{n}\sum_{j=1}^n F(x_j) \right| \geq \epsilon \right) \leq -C\epsilon^2$$

for some positive constant C. □

Observe that $\nu_y^{(n)}$ is a symmetric measure, so we have

$$\int F(x_1)\nu_y^{(n)}(dx_1,\dots,dx_n) = \int \frac{1}{n}\sum_{j=1}^n F(x_j)\nu_y^{(n)}(dx_1,\dots,dx_n) \underset{n\to\infty}{\longrightarrow} \int F(x)\alpha_\lambda(dx)$$

Theorem 2.5.5 *Let $F(x_1, \dots, x_k)$ a bounded continuous function on $\mathbb{R}^k$ and $y \in \mathcal{D}_I^o$, then*

$$\lim_{n\to\infty} \int F(x_1, \dots, x_k)\nu_y^{(n)}(dx_1, \dots, dx_n) = \int F(x_1, \dots, x_k)\alpha_\lambda(dx_1) \dots \alpha_\lambda(dx_k)$$

Proof. It is enough to consider functions of the form $F(x_1, \dots, x_k) = F_1(x_1) \dots F(x_k)$. For simplicity let us prove the case $k = 2$, the generalization to any k is straightforward. Without loosing generality, let us assume that $\int F_j(x)\alpha_\lambda(dx) = 0$. By the exchange symmetry of $\nu_y^{(n)}$ we have

$$\int F_1(x_1)F_2(x_2)\nu_y^{(n)}(dx_1, \dots, dx_n) = \int \frac{1}{n(n-1)} \sum_{i\neq j} F_1(x_i)F_2(x_j)\nu_y^{(n)}(dx_1, \dots, dx_n)$$

$$= \int \frac{n^2}{n(n-1)} \left(\frac{1}{n}\sum_i F_1(x_i)\right) \left(\frac{1}{n}\sum_j F_2(x_j)\right) \nu_y^{(n)}(dx_1, \dots, dx_n) + O\left(\frac{1}{n}\right)$$

and this last expression converges to 0 an $n \to \infty$ by (2.5.7) .

□

The generalization to more dimensions of the above results is quite straightforward and can be left as exercise. Let us state here what the result is in this context.

Let $\alpha(d\mathbf{x})$ a probability measure on $\mathbb{R}^d$ that satisfies conditions used in section 2.3. Let us assume that its characteristic function is such that $|\phi(\mathbf{k})| < 1$ for $\mathbf{k} \neq 0$, and such that $|\phi(\mathbf{k})|^r$ is integrable on $\mathbb{R}^d$ for some integer $r \geq 1$. Then, for $n \geq r$ the n-convolution of α has a density and we denote by $f_n(\mathbf{x})$ the density of the distribution of $(\mathbf{X}_1 + \cdots + \mathbf{X}_n)/n$, where $\{\mathbf{X}_j\}$ are i.i.d. with common distribution $\alpha(d\mathbf{x})$.

Theorem 2.5.6 *For any $\mathbf{y} \in \mathcal{D}_I^o$ we have*

$$\lim_{n\to\infty} \frac{1}{n} \log f_n(\mathbf{y}) = -I(\mathbf{y}) \ . \tag{2.5.8}$$

Example Let $V : \mathbb{R} \to \mathbb{R}_+$ a positive function such that $V(y) \to +\infty$ for $|y| \to +\infty$, and such that

$$Z(\lambda, \beta) = \int e^{-\beta V(y)+\lambda y} dy < \infty \qquad \forall\ \lambda \in \mathbb{R}, \beta > 0.$$

Then we can define the probability density (on $\mathbb{R}^2$)

$$f_{\lambda,\beta}(r,p) = \frac{e^{-\beta(V(r)+p^2/2)+\lambda r}}{\sqrt{2\pi\beta^{-1}}Z(\lambda,\beta)} \tag{2.5.9}$$

Let $\{Y_j = (r_j, p_j)\}$ be a sequence of i.i.d. random variables with common law given by $f_{0,\beta_0}(r,p)dr\,dp$, $\beta_0 > 0$ fixed.

Then the vector valued random variables $\mathbf{X}_j = (r_j,\ (V(r_j)+p_j^2/2))$ clearly has a law $\alpha(d\mathbf{x})$ which is degenerate in $\mathbb{R}^2$ but $\alpha * \alpha$ has a density w.r.t. the Lebesgue measure. Its logarithmic moment generating function is given by

$$\mathcal{Z}(\lambda,\eta) = \log \int e^{\lambda r+\eta(V(r)+p^2/2)} f_{0,\beta}(r,p)drdp = \log\left(\frac{Z(\lambda,\beta_0-\eta)}{Z(0,\beta_0)}\sqrt{\frac{\beta_0}{\beta_0-\eta}}\right)$$

for $\eta < \beta_0$ and $+\infty$ otherwise. The corresponding Legendre transform, for $\mathcal{L} \in \mathbb{R}$ and $U > 0$, is given by

$$\begin{aligned} I(\mathcal{L},U) &= \sup_{\eta<\beta_0,\lambda}\{\lambda\mathcal{L}+\eta U - \log\mathcal{Z}(\lambda,\eta)\} \\ &= \sup_{\beta>0,\lambda}\left\{\lambda\mathcal{L}-\beta U-\log\left(\sqrt{2\pi\beta^{-1}}Z(\lambda,\beta)\right)\right\}+\beta_0 U+\log\left(\sqrt{2\pi\beta_0^{-1}}Z(0,\beta_0)\right) \end{aligned}$$

The function defined by

$$S(U,\mathcal{L}) = \inf_{\lambda,\beta>0}\left\{-\lambda\mathcal{L}+\beta U-\log\left(Z(\lambda,\beta)\sqrt{2\pi\beta^{-1}}\right)\right\} \tag{2.5.10}$$

is called *thermodynamic entropy*. So we have obtained

$$I(\mathcal{L},U) = -S(U,\mathcal{L})+\beta_0 U+\log Z(0,\beta_0)+\frac{1}{2}\log\frac{2\pi}{\beta_0}$$

Observe that S does not depend on β_0.

The density of the distribution of $\frac{1}{n}\sum_{j=1}^n \mathbf{X}_j$ is given by

$$\begin{aligned} &f_n(\mathcal{L},U) \\ &= \int_{\mathbb{R}^{2n}} \frac{e^{-\beta_0\sum_j \mathcal{E}_j}}{(2\pi\beta_0^{-1})^{n/2}Z(0,\beta_0)^n}\delta\left(\frac{1}{n}\sum_{j=1}^n \mathcal{E}_j - U; \frac{1}{n}\sum_{j=1}^n r_j - \mathcal{L}\right)\prod_j dr_j dp_j \\ &= \frac{e^{-n\beta_0\mathcal{E}}}{(2\pi\beta_0^{-1})^{n/2}Z(0,\beta_0)^n}\int_{\mathbb{R}^{2n}}\delta\left(\frac{1}{n}\sum_{j=1}^n \mathcal{E}_j - U; \frac{1}{n}\sum_{j=1}^n r_j - \mathcal{L}\right)\prod_j dr_j dp_j \\ &= \frac{e^{-n\beta_0\mathcal{E}}}{(2\pi\beta_0^{-1})^{n/2}Z(0,\beta_0)^n}\Gamma_n(\mathcal{L},U). \end{aligned}$$

where $\Gamma_n(r, \mathcal{E})$ is the volume of the corresponding microcanonical $2n-2$-dimensional surface on $\mathbb{R}^{2n}$. More precisely, using the co-area formula [4],

$$\Gamma_n(\mathcal{L}, U) = \int_{\Sigma(nU, n\mathcal{L})} \frac{1}{\sum_j^n (p^2 + V'(r_i)^2)} d\sigma(r_1, p_1, \dots, r_n, p_n) \tag{2.5.11}$$

where $d\sigma$ is the $2n-2$-dimensional surface (Hausdorff) measure of the microcanonical manifold

$$\Sigma_n(nU, n\mathcal{L}) = \left\{ \sum_{i=1}^n \mathcal{E}_i = nU, \ \sum_{i=1}^n r_i = n\mathcal{L} \right\} \tag{2.5.12}$$

Applying (2.5.8) we obtain

$$\lim_{n \to \infty} \frac{1}{n} \log \Gamma_n(\mathcal{L}, U) = S(U, \mathcal{L}) \ . \tag{2.5.13}$$

for any $(\mathcal{L}, U) \in \mathcal{D}_S^o$. A sufficient condition to have $\mathcal{D}_S^0 = \mathbb{R} \times (0, \infty)$ is $V(r) \geq cr^2$ for a positive constant c.

Chapter 3

Statistical mechanics and thermodynamics of one dimensional chain of oscillators

3.1 The model: grand canonical formalism

We study a system of n anharmonic oscillators. The particles are denoted by $j = 1, \dots n$. We denote with $q_j, j = 1, \dots, n$ 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 *wall*, 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

$$Z(\lambda, \beta) := \int e^{-\beta V(r) + \lambda r} dr < +\infty \tag{3.1.1}$$

for all $\beta > 0$ and all $\lambda \in \mathbb{R}$. Let a be the equilibrium interparticle spacing, where V attains its minimum that we assume is 0: $V(a) = 0$. It is convenient to work with interparticle distance as coordinates, rather than absolute particle position, so we define $\{r_j = q_j - q_{j-1} - a,\ j = 1, \dots, n\}$. Without loosing any generality, we will choose $a = 0$ for the sequence.

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

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

where

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

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.

At the other end of the chain we apply a constant force $\tau \in \mathbb{R}$ on the particle n (tension). The position of the particle n is given by $q_n = \sum_{j=1}^n r_j$. We consider the Hamiltonian dynamics:

$$\begin{aligned}
&\dot{r}_j(t) = p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, n, \\
&\dot{p}_j(t) = V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j = 1, \dots, n-1, \\
&\dot{p}_n(t) = \tau - V'(r_n(t)),
\end{aligned} \tag{3.1.2}$$

It is easy to see that, for any $\beta > 0$, the grand canonical measure $\mu^{gc}_{\tau,\beta}$ defined by

$$d\mu^{n,gc}_{\tau,\beta} = \prod_{j=1}^n \frac{e^{-\beta(\mathcal{E}_j - \tau r_j)}}{\sqrt{2\pi\beta^{-1}}Z(\beta\tau, \beta)} dr_j dp_j \tag{3.1.3}$$

is stationary for this dynamics. The distribution $\mu^{n,gc}_{\tau,\beta}$ is called grand canonical Gibbs measure at temperature $T = \beta^{-1}$ and tension (or pressure) τ. Notice that $\{r_1, \dots, r_n, p_1, \dots, p_n\}$ are independently distributed under this probability measure.

We have already defined the *thermodynamic entropy* in the previous chapter as

$$S(U, \mathcal{L}) = \inf_{\lambda,\beta>0} \left\{ -\lambda\mathcal{L} + \beta U - \log\left(Z(\lambda, \beta)\sqrt{2\pi\beta^{-1}} \right) \right\} \tag{3.1.4}$$

Observe that $\Gamma_n(\mathcal{L}, U)$ is clearly sub–multiplicative

$$\Gamma_{n+m}(\mathcal{L}, U) \geq \Gamma_n(\mathcal{L}, u)\Gamma_m(\mathcal{L}, U)$$

that implies the existence of the limit

$$\lim_{n\to\infty} \frac{1}{n} \log \Gamma_n(\mathcal{L}, U) = S(U, \mathcal{L}) \ . \tag{3.1.5}$$

and applying (2.5.8) we identify as the thermodynamic entropy defined by (3.1.4).

This is the fundamental relation that connects the microscopic system to its thermodynamic macroscopic description.

The limit in (3.1.5) is intended for all avalues of the internal energy $U > 0$. It is easy to see that $S(U, \mathcal{L}) > 0$, and we extend its definition to the value $U = 0$ by setting $S(0, \mathcal{L}) = 0$.

It is easy to prove from (2.5.10) and (3.1.5) that $S(U, \mathcal{L})$ is concave and homogeneous of degree 1.

We can now define the other thermodynamic quantities from the entropy definition (3.1.4). From equation (3.1.4) we have

$$\lambda(\ell, u) = -\frac{\partial S(\ell, u)}{\partial \ell}, \qquad \beta(\ell, u) = \frac{\partial S(\ell, u)}{\partial u} \tag{3.1.6}$$

and we will always define the tension as $\tau(\ell, u) = \lambda(\ell, u)/\beta(\ell, u)$.

$$\begin{aligned} \ell(\lambda, \beta) &= \frac{\partial \log Z(\lambda, \beta)}{\partial \lambda} = \int r \, \frac{e^{\lambda r - \beta V(r)}}{Z(\lambda, \beta)} \, dr = \int r_j \, d\mu^{gc}_{\tau,\beta} \\ u(\lambda, \beta) &= -\frac{\partial \log \left(Z(\lambda, \beta)\sqrt{2\pi/\beta} \right)}{\partial \beta} = \int V(r) \frac{e^{\lambda r - \beta V(r)}}{Z(\lambda, \beta)} \, dr + \frac{1}{2\beta} = \int \mathcal{E}_j \, d\mu^{gc}_{\tau,\beta} \end{aligned} \tag{3.1.7}$$

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

$$dS = -\beta\tau d\ell + \beta du = \frac{đQ}{T} \tag{3.1.8}$$

where $đQ$ is the (non-exact) differential

$$đQ = -\tau d\ell + du \tag{3.1.9}$$

and represents the energy gained (or lost) by the system under the infinitesimal change $d\ell, du$. In fact $\tau d\ell$ is the infinitesimal *work* done on the system by the force τ to perform the infinitesimal displacement $d\ell$, while du is the infinitesimal change of *internal energy*, so that we can identify $đQ$ as the energy exchanced from the system to the *exterior* during the *thermodynamic* infinitesimal change $d\ell, du$.

3.2 Microcanonical measure

Instead of applying a force (tension) to one side of the chain, one can fix the particle n to another wall at distance nr ($q_n = \sum_{j=1}^n r_j = nr$ and $p_n = \dot{p}_n = 0$). The corresponding constrained dynamics is

$$\begin{aligned} \dot{r}_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \ldots, n-1, \\ \dot{p}_j(t) &= V'(r_{j+1}(t)) - V'(r_j(t)), \qquad j = 1, \ldots, n-1, \\ r_n(t) &= nr - \sum_{j=1}^{n-1} r_j(t) \; . \end{aligned} \tag{3.2.1}$$

The dynamics now is conserving the total energy $\mathcal{H} = \sum_j \mathcal{E}_j = nu$ and the total length $\sum_{j=1}^n r_j = nr$. The microcanonical measures $\mu_{r,u}^{n,mc}$ are now stationary for this dynamics. These are defined in the following way:

Consider the vector valued i.i.d. random variables

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

distributed by $d\mu_{\tau_0,\beta_0}^{n,gc}$. Fix $\mathbf{x} = (r, u)$, and define $\mu_{\mathbf{x}}^{n,mc}$ 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

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

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

The multidimensional application of theorem 2.5.4 gives the following *equivalence between microcanonical and grandcanonical measure*:

Theorem 3.2.1 *Given* $\mathbf{x} = (r, u)$, *let*

$$\beta = \beta(r, u), \qquad \tau = \lambda(r, u)\beta^{-1}.$$

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

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

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

Theorem 3.2.2 *Under the same conditions of Theorem 3.2.1, assume that*

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

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 follows the argument used for Theorems 2.5.4 and 2.5.5.

3.3 Canonical measure

Applying a Langevin's thermostat at temperature $T = \beta^{-1}$ to the particle n (or to any other particle), we obtain a dynamics that has the canonical measure $\mu^{n,c}_{r,\beta}$ as stationary measure:

$$\begin{aligned} \dot r_j(t) &= p_j(t) - p_{j-1}(t), \qquad j = 1, \dots, n-1, \\ dp_j(t) &= (V'(r_{j+1}(t)) - V'(r_j(t)))\, dt \\ &\qquad\qquad + \delta_{j,n-1}\left(-p_j(t)dt + \sqrt{\beta}dw(t)\right), \qquad j = 1, \dots, n-1, \\ r_n(t) &= nr - \sum_{j=1}^{n-1} r_j(t)\ . \end{aligned} \tag{3.3.1}$$

This is defined as follows:

If we condition the grand canonical measure $\mu^{n,gc}_{0,0,\beta}$ on the total length of the chain equal to $L = nr = \sum_j r_j = q_n - q_0$, we obtain the canonical measure that we denote by $\mu^{n,c}_{r,\beta}$. We can formally write

$$d\mu^{n,c}_{r,\beta} = \prod_j \frac{e^{-\beta p_j^2/2}}{\sqrt{2\pi\beta^{-1}}} dp_j \otimes \frac{e^{-\beta \sum_j V(r_j)}}{Z_{n,c}(r,\beta)} \delta\left(\sum_j r_j = nr\right) \prod_j dr_j$$

where $Z_{n,c}(r,\beta)$ is the normalization constant (canonical partition function).

Similar statements as theorems 3.2.1 and 3.2.2 holds, $\mu^{n,c}_{r,\beta}$ converging to the grand-canonical measure $\mu^{n,gc}_{\tau,\beta}$, with τ given by the thermodynamic relations (3.1.6).

Other boundary conditions can be made, like applying a tension τ and a Langevin thermostat at temperature β^{-1} to the n particle, obtaining a system with $\mu^{gc}_{\tau,\beta}$ as stationary measure.

3.4 Local equilibrium, local Gibbs measures

The Gibbs distributions defined in the above sections are also called 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 precise mathematical definition, that will be useful later for proving macroscopic behaviour of the system.

Definition 3.4.1 *Given two functions $\beta(y) > 0, \tau(y), y \in [0,1]$, 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 $y \in (0,1)$,*

$$\lim_{n\to\infty} \mu_n\big|_{([ny],[ny]+k)} = \mu^{k,gc}_{\tau(y),\beta(y)} \tag{3.4.1}$$

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:

$$\prod_{j=1}^{n} \frac{e^{-\beta(j/n)(\mathcal{E}_j - \tau(j/n) r_j)}}{\sqrt{2\pi\beta(j/n)^{-1}}Z(\beta(j/n)\tau(j/n), \beta(j/n))} dr_j dp_j = g^n_{\tau(\cdot),\beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j \tag{3.4.2}$$

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

$$e^{\sum_j F_j(r_{j-h},p_{j-h},\dots,r_{j+h},p_{j+h})/n} g^n_{\tau(\cdot),\beta(\cdot)} \prod_{j=1}^{n} dr_j dp_j \tag{3.4.3}$$

where F_j are local functions.

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

$$S(r(\cdot), u(\cdot)) = \int_0^1 S(r(y), u(y))\, dy \tag{3.4.4}$$

where $r(y), u(y)$ are computed from $\tau(y), \beta(y)$ using (3.1.7).

Chapter 4

Entropy

4.1 Generalities

Let Ω be a polish space and $\mathcal{P}(\Omega)$ the topological space of probability measures on Ω equipped with the weak topology. For $\mu, \nu \in \mathcal{P}(\Omega)$, the relative entropy $H(\nu|\mu) \in [0, \infty]$ of μ with respect to ν is defined by

$$H(\nu|\mu) = \sup_f \left\{ \int f d\nu - \log \left(\int e^f d\mu \right) \right\} \tag{4.1.1}$$

where the supremum is taken over all bounded continuous functions $f : \Omega \to \mathbb{R}$. The positivity of $H(\nu|\mu)$ follows from the choice $f = 0$ in the variational formula. Observe also that the supremum can be restricted to the set of positive bounded continuous functions.

As a trivial but useful consequence we have the following entropy inequality

Proposition 4.1.1 (Entropy inequality) *Let $f : \Omega \to \mathbb{R}$ be a bounded measurable function and $\eta > 0$ a positive number. Then*

$$\int f d\nu \leq \eta^{-1} \left\{ \log \left(\int e^{\eta f} d\mu \right) + H(\nu|\mu) \right\} \tag{4.1.2}$$

Proof If f is continuous it is a trivial consequence of the definition. Since the class of f's for which (4.1.2) holds is closed under point-wise convergence, (4.1.2) continues to be true for every bounded measurable function. □

Proposition 4.1.2 *Relative entropy is convex and lower semicontinuous.*

Proof It is a simple consequence of the variational formula. □

Proposition 4.1.3 *The entropy $H(\nu|\mu)$ is equal to $+\infty$ if ν is not absolutely continuous with respect to μ. Otherwise it is given by*

$$H(\nu|\mu) = \int \phi \log \phi d\mu, \quad \phi(x) = \left(\frac{d\nu}{d\mu}\right)(x) \tag{4.1.3}$$

*P*roof Observe first that for any density function ϕ the integral of $\phi \log \phi$ makes sense in $\mathbb{R} \cup \{+\infty\}$ since $x \in [0, \infty) \to x \log x$ is bounded above so that the negative part of $\phi \log \phi$ is integrable with respect to μ.

If ν is not absolutely continuous with respect to μ then there exists a measurable set A such that $\mu(A) = 0, \nu(A) > 0$. Choosing the function $f = \alpha \mathbf{1}_A, \alpha > 0$ in (4.1.2) we get $H(\nu|\mu) \geq \alpha\nu(A)$. Since α is arbitrary we have $H(\nu|\mu) = +\infty$.

We first show that if $d\nu = \phi d\mu$ is absolutely continuous with respect to μ and if $d\nu_\theta = \theta d\mu + (1-\theta)d\nu = \phi_\theta d\mu$ for $\theta \in [0, 1]$ then

$$\lim_{\theta \to 0} \int \phi_\theta \log \phi_\theta d\mu = \int \phi \log \phi d\mu \tag{4.1.4}$$

Since $x \in [0, \infty) \to x \log x$ is convex, we have

$$I(\theta) = \int \phi_\theta \log \phi_\theta d\mu \leq (1-\theta) \int \phi \log \phi d\mu$$

On the other hand since $x \in (0, \infty) \to \log x$ is concave and non-decreasing, $\log \phi_\theta \geq \sup\{\log \theta, (1-\theta)\log \phi\}$. Therefore

$$I(\theta) = \theta \int \log \phi_\theta d\mu + (1-\theta) \int \phi \log \phi_\theta d\mu \geq \theta \log \theta + (1-\theta)^2 \int \phi \log \phi d\mu$$

It proves (4.1.4).

Since $\phi_\theta \geq \theta > 0$, Jensen's inequality shows

$$\exp\left[\int \psi d\nu_\theta - I(\theta)\right] \leq \int \frac{e^\psi}{\phi_\theta} d\nu_\theta = \int \exp(\psi) d\mu$$

Hence we have

$$\int \psi d\nu_\theta \leq I(\theta) + \log\left(\int e^\psi d\mu\right)$$

It implies $H(\nu_\theta|\mu) \leq I(\theta)$. Recall that relative entropy is lower semi-continuous. In view (4.1.4) we have

$$H(\nu|\mu) \leq \int \phi \log \phi d\mu$$

To obtain the reversed inequality we observe that if ϕ is uniformly positive and uniformly bounded, it is trivial, by the variational formula defining $H(\nu|\mu)$, that

$$\int \phi \log \phi d\mu \leq H(\nu|\mu)$$

If ϕ is uniformly strictly positive but not bounded we define $\phi_n = \phi \wedge n$ and by Fatou's lemma we have

$$\begin{aligned}
&\int \phi \log \phi d\mu = \int \log \phi d\nu \\
&\leq \liminf_{n\to\infty} \int \log \phi_n d\nu \\
&\leq H(\nu|\mu) + \liminf_{n\to\infty} \log \left(\int (f \wedge n) d\mu \right) = H(\nu|\mu)
\end{aligned}$$

Finally to treat the general case we assume ϕ is uniformly bounded and use ϕ_θ defined above. We proved that $\int \phi_\theta \log \phi_\theta d\mu \leq H(\nu_\theta|\mu)$. Since $\theta \in [0,1] \to H(\nu_\theta|\mu)$ is bounded, lower semi-continuous and convex, it is continuous. Using also (4.1.4) the result follows. □

We now consider the case $\Omega = (\mathbb{R}^2)^{\mathbb{Z}}$ equipped with the product topology. The closed set of translation invariant probability measures on Ω is noted $\mathcal{T}$. Let Λ be a subset of $\mathbb{Z}$ and $\mu, \nu \in \mathcal{P}(\Omega)$. The relative entropy $H_\Lambda(\nu|\mu)$ of ν with respect to ν in Λ is defined by

$$H_\Lambda(\nu|\mu) = H(\mu_\Lambda|\nu_\Lambda) \tag{4.1.5}$$

where μ_Λ, ν_Λ are the marginals of μ and ν with respect to Λ.

Proposition 4.1.4 (Superadditivity) *Assume $\mu \in \mathcal{T}$ is product. We have the following superadditivity property of the entropy:*

$$H_{\Lambda\cup\Lambda'}(\nu|\mu) \geq H_\Lambda(\nu|\mu) + H_{\Lambda'}(\nu|\mu) \tag{4.1.6}$$

if $\Lambda \cap \Lambda' = \emptyset$.

Proof Let f_Λ (resp. $f_{\Lambda'}$) be an arbitrary continuous bounded function depending only on ω through sites in Λ (resp. Λ'). We have

$$\int f_\Lambda d\nu_\Lambda - \log \left(\int e^{f_\Lambda} d\mu_\Lambda \right) = \int f_\Lambda d\nu_{\Lambda\cup\Lambda'} - \log \left(\int e^{f_\Lambda} d\mu_{\Lambda\cup\Lambda'} \right)$$

and similarly with Λ replaced by Λ'. Summing the two equalities obtained and using independence of f_Λ and $f_{\Lambda'}$ under $\mu_{\Lambda\cup\Lambda'}$, we get

$$H_{\Lambda\cup\Lambda'}(\nu|\mu) \geq \int (f_\Lambda + f_{\Lambda'}) d\nu_{\Lambda\cup\Lambda'} - \log\left(\int e^{[f_\Lambda + f_{\Lambda'}]} d\mu_{\Lambda\cup\Lambda'}\right)$$
$$= \left\{\int f_\Lambda d\nu_\Lambda - \log\left(\int e^{f_\Lambda} d\mu_\Lambda\right)\right\} + \left\{\int f'_\Lambda d\nu'_\Lambda - \log\left(\int e^{f'_\Lambda} d\mu'_\Lambda\right)\right\}$$

Taking now the supremum over f_Λ and $f_{\Lambda'}$ we obtain the desired inequality. □

So if ν, μ are translation invariant and μ is product, denoting $\Lambda_n = \{-n, \dots, n\}$, we have that $H_{\Lambda_n}(\nu|\mu)$ is a superadditive function of n, and consequently it exists the limit

$$\bar{H}(\nu|\mu) = \lim_{n\to\infty} \frac{1}{2n+1} H_{\Lambda_n}(\nu|\mu) = \sup_n \frac{H_{\Lambda_n}(\nu|\mu)}{2n+1} \tag{4.1.7}$$

Moreover it is easy to show that $\nu \in \mathcal{T} \to \bar{H}(\nu|\mu)$ inherits properties of relative entropy. Hence it is convex and lower semicontinuous.

For any bounded continuous function ϕ with support in $\{-n_0, \dots, n_0\}$ define the limit

$$\bar{F}(\phi) = \lim_{n\to\infty} \frac{1}{2n+1} \bar{F}_n(\phi), \quad \bar{F}_n(\phi) = \log \int e^{\sum_{i=-n}^{n} \tau_i \phi}\, d\mu \tag{4.1.8}$$

where τ_i is the shift operator on functions on $(\mathbb{R}^2)^{\mathbb{Z}}$. Existence of the limit is proved in the following proposition.

Proposition 4.1.5 *Let ν a translation invariant probability on Ω, then*

$$\bar{H}(\nu|\mu) = \sup_\phi \left\{\int \phi\, d\nu - \bar{F}(\phi)\right\} \tag{4.1.9}$$

where the supremum is taken over all bounded continuous functions ϕ.

Proof We claim it is sufficient to prove that

$$\liminf_{n\to\infty} (2n+1)^{-1} \bar{F}_n(\phi) \geq \sup_{\nu\in\mathcal{T}} \left\{\int \phi d\nu - \bar{H}(\nu|\mu)\right\} \tag{4.1.10}$$

and

$$\limsup_{n\to\infty} (2n+1)^{-1} \bar{F}_n(\phi) \leq \sup_{\nu\in\mathcal{T}} \left\{\int \phi d\nu - \bar{H}(\nu|\mu)\right\} \tag{4.1.11}$$

Assume we proved (4.1.10) and (4.1.11). Let $\mathcal{M}(\Omega)$ the vector space of finite signed measures on Ω equipped with the weak topology. We extend $\bar{H}$ to $\mathcal{M}(\Omega)$ by $\bar{H}(\nu|\mu) = +\infty$ if $\mu \notin \mathcal{T}$. Since $\mathcal{T}$ is a closed convex set the function $\bar{H}$ extended in this way remains convex and lower semi-continuous. Let $(\mathcal{M}(\Omega))'$ be the topological dual of $\mathcal{M}(\Omega)$ and consider the application $\Phi \in (\mathcal{M}(\Omega))' \to f_\Phi \in C_b(\Omega)$ defined by $f_\Phi(x) = \Phi(\delta_x)$. Remark that f_Φ is continuous and that $\int f_\Phi d\nu = \Phi(\nu)$. Moreover it is injective since the finite support signed measures are dense (for the weak topology) into $\mathcal{M}(\Omega)$ (see [**?**], appendix III, theorem 4) and surjective since for any $f \in C_b(\Omega)$ the linear form $\Phi : \nu \in \mathcal{M}(\Omega) \to \int_\Omega f d\nu \in \mathbb{R}$ is such that $f_\Phi = f$. Hence $\Phi \to f_\Phi$ is an isomorphism between $(\mathcal{M}(\Omega))'$ and $C_b(\Omega)$. Then Fenchel-Moreau's theorem implies

$$\bar{H}(\nu|\mu) = \sup_\phi \left\{ \int \phi \, d\nu - \bar{F}(\phi) \right\} \tag{4.1.12}$$

for any $\nu \in \mathcal{M}(\omega)$ and in particular for $\nu \in \mathcal{T}$.

We start by proving (4.1.10). Let $\nu \in \mathcal{T}$ such that $\bar{H}(\nu|\mu) < \infty$. By the variational formula defining $H_{\Lambda_n}(\nu|\mu)$ applied with $\sum_{i=-n}^{n} \tau_i \phi$ and the translation invariance of ν we have

$$\begin{aligned} \frac{\bar{F}_n(\phi)}{2n+1} &\geq \int \frac{1}{2n+1} \left(\sum_{i=-n}^{n} \tau_i \phi \right) \, d\nu - \frac{H_{\Lambda_n}(\nu|\mu)}{|\Lambda_n|} \\ &\geq \int \phi \, d\nu - \bar{H}(\nu|\mu) \end{aligned}$$

Taking the liminf in n and the supremum over $\nu \in \mathcal{T}$ we get (4.1.10).

Observe that for any $n \geq 1$, we have

$$\log \left(\int e^{\sum_{i=-n}^{n} \tau_i \phi} d\mu \right) = \sup_\alpha \left\{ \int \left(\sum_{i=-n}^{n} \tau_i \phi \right) \, d\alpha - H_{\Lambda_{n+n_0}}(\alpha|\mu) \right\} \tag{4.1.13}$$

where the supremum is carried over all probability measures α on $(\mathbb{R}^2)^{\Lambda_{n+n_0}}$. One sense of the inequality is trivial by the variational formula defining $H_{\Lambda_{n+n_0}}(\alpha|\mu)$ and the other sense is obtained by taking the optimal α which maximizes the supremum in (4.1.13). This α is such that $H_{\Lambda_{n+n_0}}(\alpha|\mu) < +\infty$.

For such α we define $\bar{\alpha} \in \mathcal{T}$ in two steps. First α^* is obtained by taking independent copies of α on all translated disjoint cubes $(C_k)_{k \in \mathbb{Z}}$ of Λ_{n+n_0}:

$$\alpha^* = \otimes_{k \in \mathbb{Z}} \tau_{2k(n+n_0)+1} \alpha, \quad C_k = \tau_{2k(n+n_0)+1} \Lambda_{n+n_0}$$

The family of probability measures $(\alpha^p)_{p \geq 1}$ defined by

$$\alpha^p = \frac{1}{2p+1} \sum_{\ell=-p}^{p} \tau_\ell \alpha^*$$

is tight and we denote by $\bar{\alpha}$ a fixed limit point of the family. To simplify notations we denote the subsequence along which the limit is achieved by the same letter p. It is trivial that $\bar{\alpha}$ is translation invariant.

Let $B_j = \cup_{k=-j}^{j} C_k$. Since entropy is lower semicontinuous we have

$$\bar{H}(\bar{\alpha}|\mu) \leq \lim_{j\to\infty} \liminf_{p\to\infty} |B_j|^{-1} H_{B_j}(\alpha^p|\mu) \tag{4.1.14}$$

By convexity of entropy and translation invariance of μ we have

$$\begin{aligned} |B_j|^{-1} H_{B_j}(\alpha^p|\mu) &\leq \frac{1}{\Lambda_{n+n_0}} \frac{1}{(2p+1)(2j+1)} \sum_{\ell=-p}^{p} H_{B_j}(\tau_\ell \alpha^*|\mu) \\ &= \frac{1}{\Lambda_{n+n_0}} \frac{1}{(2p+1)(2j+1)} \sum_{\ell=-p}^{p} H_{\tau_{-\ell} B_j}(\alpha^*|\mu) \end{aligned}$$

Observe that $\tau_{-\ell} B_j$ can be written as the disjoint union $I \cup \cup_{k=j_\ell}^{j_\ell+2j-2} C_k \cup F$ where $j_\ell \in \mathbb{Z}$, $I \subset C_{j_\ell - 1}$ and $F \subset C_{j_\ell+2j-1}$.

Since the relative entropy of a product of measures $\beta \otimes \gamma$ is the sum of the relative entropies of β and γ, we have

$$\begin{aligned} H_{\tau_{-\ell} B_j}(\alpha^*|\mu) &= H_I(\alpha^*|\mu) + \sum_{k=j_\ell}^{j_\ell+2j-2} H_{C_k}(\alpha^*|\mu) + H_F(\alpha^*|\mu) \\ &= H_I(\alpha^*|\mu) + (2j-1) H_{\Lambda_{n+n_0}}(\alpha^*|\mu) + H_F(\alpha^*|\mu) \end{aligned}$$

Since $H_I(\alpha^*|\mu) \leq H_{\Lambda_{n+n_0}}(\alpha|\mu)$ and $H_F(\alpha^*|\mu) \leq H_{\Lambda_{n+n_0}}(\alpha|\mu)$, taking first the limit in p and then the limit in j we get

$$\bar{H}(\bar{\alpha}|\mu) \leq \frac{H_{\Lambda_{n+n_0}}(\alpha|\mu)}{|\Lambda_{n+n_0}} \tag{4.1.15}$$

Moreover it is clear that

$$\lim_{n\to\infty} \left| \frac{1}{2n+1} \sum_{i=-n}^{n} \int (\tau_i \phi)\, d\alpha - \int \phi d\bar{\alpha} \right| = 0$$

and we get (4.1.11). $\square$

4.2 Entropy Production

Let $(\omega_t)_{t\geq 0}$ be a Markov process on $\Omega_\Lambda = (\mathbb{R}^2)^\Lambda$, $\Lambda \subset \mathbb{Z}$, with generator L_Λ and invariant probability measure μ. We denote by A_Λ (resp. S_Λ) the antisymmetric (resp. symmetric) part of L_Λ in $\mathbb{L}^2(\Omega_\Lambda, \mu)$. We assume the space of smooth bounded functions on Ω_Λ is a common core of A_Λ and S_Λ and that $L_\Lambda = A_\Lambda + S_\Lambda$ and $L^*_\Lambda = -A_\Lambda + S_\Lambda$ are generators of Feller semigroups $(P^t_\Lambda)_{t\geq 0}$ and $(P^{*t}_\Lambda)_{t\geq 0}$. We suppose that L_Λ (resp. S_Λ) can be extended to strong Feller semigroups on $\mathbb{L}^2(\Omega_\Lambda, \mu)$. The semigroup generated by L_Λ (resp. L^*_Λ on $\mathbb{L}^2(\Omega_\Lambda, \mu)$) is also denoted P^t_Λ (resp. P^{*t}_Λ).

The first proposition below shows that entropy w.r.t. invariant probability measures can only decrease

Proposition 4.2.1 *For any probability measure ν on Ω_Λ we have*

$$H(\nu P^t_\Lambda|\mu) \leq H(\nu|\mu) \tag{4.2.1}$$

Proof By definition we have

$$H(\nu P^t_\Lambda|\mu) = \sup_\phi \left\{ \int P^t_\Lambda \phi d\nu - \log\left(\int e^\phi d\mu \right) \right\}$$

and by Jensen's inequality and stationarity of μ we have

$$\int e^{P^t_\Lambda \phi} d\mu = \int d\mu(\omega) \exp\left(\mathbb{E}_\omega(\phi(\omega_t)) \right) \leq \int \mathbb{E}_\omega(e^{\phi(\omega_t)}) d\mu(\omega) = \int e^\phi d\mu$$

and then the result follows since $P^t_\Lambda \phi$ is a bounded continuous function. □

In particular this shows that if we start from a probability measure ν with finite entropy then at any time the probability measure νP^t_Λ has finite entropy and hence is absolutely continuous with respect to μ. Let $g_\Lambda(t)$ be the density of νP^t_Λ w.r.t. μ.

We are now interested in the entropy production rate. The Dirichlet form of ν w.r.t. μ is defined by

$$D_\Lambda(\nu|\mu) = \sup \left\{ -\int \frac{S_\Lambda \psi}{\psi} d\nu \;:\; \psi \in \mathrm{Dom}(S_\Lambda), \inf \psi > 0 \right\} \tag{4.2.2}$$

Proposition 4.2.2 *Let ν be a probability measure on Ω_Λ with finite entropy $H(\nu|\mu) = H_\Lambda(\nu|\mu) < \infty$. For every $t, h \geq 0$, we have that*

$$H(\nu P^{t+h}_\Lambda|\mu) - H(\nu P^t_\Lambda|\mu) \leq 2 \int_t^{t+h} ds D_\Lambda(\nu P^s_\Lambda|\mu) \tag{4.2.3}$$

Proof Let α and β two probability measures on Ω_Λ. Jensen's inequality shows that

$$H(\alpha P^t_\Lambda|\beta P^t_\Lambda) \leq H(\alpha|\beta) \tag{4.2.4}$$

It is sufficient to show the proposition for $t = 0$. Let ψ be a smooth bounded positive function with mean one with respect to μ. Fix a positive time τ. We define the probability measure β by $d\beta = \psi d\mu$. Then we have βP_Λ^τ is absolutely continuous with respect to μ with density $P_\Lambda^{*\tau}\psi$.

It is an elementary fact that

$$H(\alpha|\beta) = H(\alpha|\mu) - \int \log\psi \, d\alpha \tag{4.2.5}$$

It follows that

$$H(\alpha P_\Lambda^t|\beta P_\Lambda^t) = H(\alpha P_\Lambda^\tau \mu) - \int \log(P_\lambda^{*\tau}\psi \, d(\alpha P_\Lambda^\tau) \tag{4.2.6}$$

Hence, with (4.2.4), we get

$$\begin{aligned} H(\alpha|\mu) - H(\alpha P_\Lambda^\tau|\mu) &\geq \int \log\psi \, d\alpha - \int P_\Lambda^\tau \log\left(P_\Lambda^{*\tau}\psi\right) \, d\alpha \\ &\geq \int \log\psi \, d\alpha - \int \log\left(P_\Lambda^\tau P_\Lambda^{*\tau}\psi\right) \, d\alpha \\ &\geq -\int \log\left(\frac{P_\Lambda^\tau P_\Lambda^{*\tau}\psi}{\psi}\right) d\alpha \\ &\geq \int \left(\frac{\psi - P_\Lambda^\tau P_\Lambda^{*\tau}\psi}{\psi}\right) d\alpha \end{aligned}$$

where we used Jensen's inequality and $\log(1+\eta) \leq \eta$.

Since $(P_\Lambda^t)_{t\geq 0}$ and $(P_\Lambda^{*t})_{t\geq 0}$ are Feller semigroups we have

$$\psi - P_\Lambda^\tau P_\Lambda^{*\tau}\psi = \psi - P_\Lambda^\tau\psi - \psi - P_\Lambda^\tau(P_\Lambda^{*\tau}\psi - \psi) = -2\tau S_\Lambda\psi + \tau\varepsilon(\psi,\tau)$$

where $\|\varepsilon(\psi,\tau)\|_\infty \to 0$ as $\tau \to 0$.

Let be $t > 0$ and divide the time interval $[0, t]$ in m small intervals of length $\tau = t/m$ and let m goes to infinity. We have

$$\begin{aligned} H(\alpha|\mu) - H(\alpha P_\Lambda^t|\mu) &= \sum_{i=0}^{m-1} \left[H(\alpha P_\Lambda^{\frac{i}{m}t}|\mu) - H(\alpha P_\Lambda^{\frac{i+1}{m}t}|\mu)\right] \\ &\geq \limsup_{m\to\infty} \sum_{i=0}^{m-1} \left[H(\alpha P_\Lambda^{\frac{i}{m}t}|\mu) - H(\alpha P_\Lambda^{\frac{i+1}{m}t}|\mu)\right] \\ &\geq \limsup_{m\to\infty} \left[-\frac{2t}{m}\sum_{i=0}^{m-1} \int \left(P_\Lambda^{\frac{it}{m}}\left(\frac{S_\Lambda\psi}{\psi}\right)\right) d\alpha + t\varepsilon(\psi, t/m))\right] \\ &= -2\int_0^t ds \int P_\Lambda^s\left(\frac{S_\Lambda\psi}{\psi}\right) d\alpha \end{aligned}$$

By taking the supremum over all ψ considered we conclude the proof. □

Proposition 4.2.3 (Donsker-Varadhan) *Let Λ be a finite set. Assume that $D_\Lambda(\nu|\mu)$ is finite and that ν is abolutely continuous with respect to μ with a density denoted by g. Then $\sqrt{g}$ belongs to the domain of $(-S_\Lambda)^{1/2}$ and*

$$D_\Lambda(\nu|\mu) = \sum_{x\in\Lambda} \int d\mu((-S_\Lambda)^{1/2}\sqrt{g})^2 \tag{4.2.7}$$

Proof See theorem 5 in [**?**]. □

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