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Energy and Density Distortion in an Oscillator Chain

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Chapter 1

Introduction

1.1 Oscillator Chains

Non equilibrium phenomena are incredibly widespread and characterize our surrounding world from its microscopic to its macroscopic aspects. Still a complete theory for these kinds of systems is not yet achieved and, in particular, non equilibrium statistical mechanics is not as well developed as its equilibrium counterpart [1,2].

One of the reason for this lack of success is given by the difficulties one encounters when it comes to give a full description of these phenomena: non equilibrium observables require in fact a bigger amount of information compared to the equilibrium ones so the task is actually more complicated [3,4].

In this thesis we deal with one of the most studied and most basic models of both equilibrium and non equilibrium statistical mechanics: a chain of oscillators.

This ideal system consists of a one-dimensional chain of point particles (called *oscillators*) which are linked to each other through a potential which is usually, but not always, harmonic (in this case we call them *harmonic oscilla-*

tors).

The Hamiltonian that describes a chain of N particles is

$$H = T + V = \frac{1}{2}\sum_{i=1}^{N} m_i v_i^2 + \frac{1}{2}\sum_{i,j=1}^{N} k\Phi_{ij} x_i x_j \tag{1.1}$$

where x_i and v_i are respectively the Cartesian coordinate and velocity of the i-th particle, m_i is its mass, k the elastic constant (which is usually the same for all particles) and $\Phi_{ij} x_i x_j$ is the potential energy where the explicit form of Φ_{ij} depends on the kind of potential (as it will be explained in the following sections).

N can be finite or infinite and the edges can be fixed, free or with periodic boundary conditions. It is important to underline that, both in equilibrium and non equilibrium situations, the boundary conditions have a significant role in determining the properties of the chain, even for a large number of particles.

That means that the influence of the system boundary is strong in all the points in the chain, whereas normally it should decay at a few correlation length from the ends of the chain [5,6,7].

This is a peculiar feature of this 1-dimensional physical system: in fact it does not occur in 2 or 3 dimensional grids of particles [8]. This is the reason why we are going to put a great emphasis on the boundary conditions that describe the system.

1.2 Equilibrium Conditions

1.2.1 Gibbs' Ensemble

In the equilibrium case one usually considers a chain with a fixed edge and with the other one in contact with a heat bath, or *reservoir*, at a temperature

T. The reservoir has an infinite heat capacity and this is usually done by considering it as made by an infinite number of oscillators [1].

Here the chain is a system which has a fixed number of particles, volume and temperature (which is the same as the heat bath): these are the characteristics of what is described by a *canonical ensemble*, at equilibrium

Before explaining this, it is better to give a quick review of the Gibbs' ensemble theory [9]. It is used in statistical mechanics to deal with systems consisting in a huge number of particles (the order of the Avogadro's number $N \approx 10^{23}$), where it is impossible to solve the equations of motion of every single particle.

We know that to define a macroscopic state we need to know all the positions and the velocities of all particles, which means all the microscopic states.

An ensemble is a set of microscopic states that satisfies some macroscopical constraints, which means that correspond to the same macroscopic state. In particular, a canonical ensemble is a set of all microscopic states with a fixed number of molecules, volume and temperature: a chain of oscillators in equilibrium with a heat bath is a typical example of this kind of ensemble.

These microscopic states "live" in the *phase space*, a space whose coordinates are the Cartesian coordinates and the momenta. Every point in this space represents a microspic state and these points are distributed following a probability distribution which depends on the type of ensemble.

In our case, the canonical one, the distribution is given by

$$f(x,v) = \frac{e^{-\beta H(x,v)}}{\int e^{-\beta H(x,v)} dx dv} = \frac{e^{-\beta H(x,v)}}{Z} \tag{1.2}$$

with $\beta = \frac{1}{k_B T}$, $k_B = 1.38 \times 10^{-23} J/K$ the Boltzmann constant and Z is the *partition function* and it is used for the normalization. The integral is computed in the phase space coordinates, which in our case will be the positions x and the velocities v, equivalent to the momenta $p = mv$, since in the numerical calculations the mass will be equal to 1.

If we want to compute the expectation value of an observable A according to the distribution of the canonical ensemble we can use the following definition

$$\langle A \rangle = \int A(x,v) f(x,v) dxdv = \frac{\int A(x,v) e^{-\beta H(x,v)} dxdv}{Z} \tag{1.3}$$

Consequently all the observables of this system (such as the energy, the average position of the particles...) will be computed following the formula (1.3).

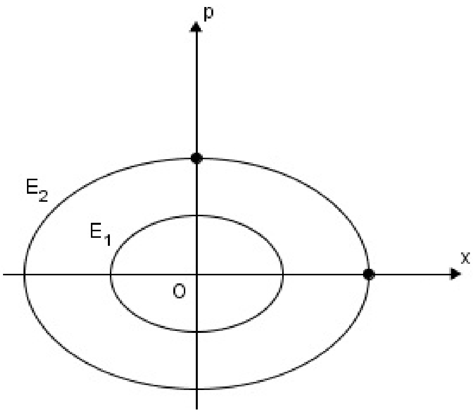


Figure 1.1: A one-dimensional harmonic oscillator in the phase space. The different levels represent different energies of the system.

1.3 Non Equilibrium Conditions

In non equilibrium conditions, two reservoirs at different temperature are usually situated at the edges of the chain: this causes a temperature gradient along a chain which is translated in a heat flux going from the hotter reservoir to the colder one through the chain. In the following sections we are going to illustrate different methods, analytical and/or numerical, used to study this system.

1.3.1 Molecular Dynamics

One of the most widespread methods used to study numerically non equilibrium problems is *molecular dynamics* which is is a computer simulation method for studying the physical movements of atoms and molecules.

The aim of this procedure is to solve the Newton's equations of motion that describe the system usually to get the trajectories of the particles. MD is actually meant to perform in the microcanonical ensemble but various algorithm have been developed that that allow us to investigate systems that are described by the canonical ensemble.

One of the most important of these algorithms is the *Nosé-Hoover algorithm* and it is used for systems in contact with a heat bath [10,11].

This extended system method was originally introduced by Nosé and subsequently developed by Hoover [12]. Usually the equations of motion concern just the system, namely the chain: the idea is to consider the heat bath as an integral part of the system by addition of an artificial variable $\tilde{s}$ in the equation of motion, associated with a mass $Q > 0$ and a velocity $\tilde{\dot{s}}$.

The Lagrangian for the extended system is [10]

$$\mathcal{L} = \sum_i \frac{m_i}{2} \tilde{s}^2 \tilde{\dot{\mathbf{x}}}_i^2 - U(\tilde{\mathbf{x}}) + \frac{1}{2} Q \tilde{\dot{s}}_i^2 - g k_B T_0 \ln \tilde{s} \tag{1.4}$$

where the first two terms are the kinetic and the potential energy, the third term is the kinetic energy of $\tilde{s}$ and the last is its potential (which ensure that the algorithm is canonical) and $g = N_{df}$.

The corresponding equations of motion are

$$\tilde{\ddot{\mathbf{x}}}_i = \frac{\tilde{\mathbf{F}}_i}{m_i \tilde{s}^2} - \frac{2 \tilde{\dot{s}} \tilde{\dot{\mathbf{x}}}_i}{\tilde{s}} \tag{1.5}$$

$$\ddot{\tilde{s}} = \frac{1}{Q\tilde{s}}\left(\sum_i m_i \tilde{s}^2 \dot{\tilde{\mathbf{x}}}_i^2 - g k_B T_0\right) \tag{1.6}$$

These equations sample a microcanonical ensemble in the extended system $(\tilde{\mathbf{x}}, \tilde{\mathbf{p}}, \tilde{s})$, that is because in the microcanonical ensemble the energy is conserved; this means that while the chain alone cannot be considered as a microcanonical ensemble, the chain and the reservoirs together can, since the energy is actually conserved in this *whole* new system.

However, the energy of the chain is not constant: accompanying the fluctuations of $\tilde{s}$ heat transfers occur between the system and the heat bath, which regulate the system temperature. These equations of motion sample a canonical ensemble in the real system. The basic Nose-Hoover algorithm is used to study chains in thermodynamic equilibrium but with some modifications can be easily extended to non equilibrium systems [12].

1.3.2 Stochastic Kernel

We have seen in the previous section that it is possible to solve numerically the equations of motion concerning the chain of oscillators to extrapolate some properties of the system. What can we say about the analytical solutions?

It is important to underline that a complete analytical theory on the harmonic oscillator chain in non equilibrium conditions already exists thanks to the work of Rieder, Lebowitz and Lieb in [13], where the method of *stochastic kernel* is used [14].

The aim of this method is to get a generalized Liouville equation, that is usually used to describe the evolution of the phase space ensemble density, when the system is in non equilibrium conditions. The interaction of the chain with the reservoirs is considered an impulsive interaction and the Langevin equation is written as

$$\frac{\partial\mu(x,t)}{\partial t}+(\mu,H)_x=\int_{x'}[K(x,x')\mu(x')-K(x',x)\mu(x)]dx' \tag{1.7}$$

where $K(x',x)$ is the transition probability density in the phase space of the system: it tells us the probability that the point of the system in the location x will be thrown into the volume element dx' by one of these impulsive interactions.

Knowing the Hamiltonian of the system is given by

$$H=T+V=\frac{1}{2}\sum_{i=N+1}^{2N}x_i^2+\frac{1}{2}\sum_{i,j=1}^{N}\Phi_{ij}x_ix_j \tag{1.8}$$

where now the potential $\Phi_{ij}x_ix_j$ is harmonic, then the generalized Liouville equation can be written as

$$\frac{\partial\mu(x,t)}{\partial t}=\sum_{i=1}^{2N}\frac{\partial}{\partial x_i}\xi_i\mu+\frac{1}{2}\sum_{i,j=1}^{2N}\frac{\partial^2}{\partial x_i\partial x_j}d_{ij}\mu \tag{1.9}$$

with

$$\xi_i=\sum_{j=1}^{2N}a_{ij}x_j \tag{1.10}$$

and

$$\mathbf{a}=\begin{pmatrix}\mathbf{0} & -\mathbf{I}\\ \mathbf{\Phi} & \mathcal{R}\end{pmatrix}\quad\text{and}\quad\mathbf{d}=\begin{pmatrix}\mathbf{0} & \mathbf{0}\\ \mathbf{0} & \epsilon\end{pmatrix} \tag{1.11}$$

with $\mathcal{R}_{ij}=\lambda_\alpha\delta_{\alpha i}\delta_{ij}$, $\lambda_\alpha=\rho_\alpha A_\alpha(8m_\alpha kT_\alpha/M_\alpha^2)^{(1/2)}$, A_α the collision cross section of the α-th piston and $\epsilon_{ij}=2kT_i\mathcal{R}_{ij}$. Since we are interested in the stationary solutions we put in (1.9) $\partial\mu/\partial t=0$ and we obtain

$$\mu_s(x)=(2\pi)^{-N}\mathrm{Det}[\mathbf{b}^{-\frac{1}{2}}]\mathrm{exp}\left[-\frac{1}{2}\sum_{i,j=1}^{2N}\mathbf{b}_{ij}^{-1}x_ix_j\right] \tag{1.12}$$

where $\mathbf{b}$ is the covariance matrix written as

$$\mathbf{b} = \begin{pmatrix} \mathbf{x} & \mathbf{z} \\ \mathbf{z}^\dagger & \mathbf{y} \end{pmatrix} \tag{1.13}$$

with

$$x_{ij} = \langle q_i q_j \rangle \text{ and } y_{ij} = \langle p_i p_j \rangle \text{ and } z_{ij} = \langle q_i p_j \rangle \tag{1.14}$$

where q_i is the displacement from the equilibrium position of the i-th particle and p_i its momentum.

Hence if know the values of the matrix we can get the kinetic temperature and the flux of the system.

To have the explicit solutions for the matrix $\mathbf{b}$ one has to solve the following matrix equations

$$\mathbf{Z} = -\mathbf{Z}^\dagger \tag{1.15}$$

$$\mathbf{Y} = \mathbf{XG} + \mathbf{ZR} \tag{1.16}$$

$$2\mathbf{E} - \mathbf{YR} - \mathbf{RY} = \nu[\mathbf{GZ} - \mathbf{ZG}] \tag{1.17}$$

and then, by using the following relations

$$kT(j, \nu; N) = \langle p_j^2 \rangle = \langle x_i \partial H / \partial x_i \rangle \tag{1.18}$$

$$j_{i-1,i} = \omega^2 \langle q_{i-1} p_i \rangle = \omega^2 Z_{12} \equiv J \tag{1.19}$$

we can compute the kinetic temperature T and the flux J which is the same for all particles.

It is important to stress that the concept of temperature is based on the distribution of the canonical ensemble average with respect to the whole system. This ensemble is defined only in equilibrium conditions, so in this case the temperature can be defined on the distribution of partial energy: in this case we talk about local or kinetic temperature, to distinguish it from the equilibrium case.

1.3.3 Langevin Equations

Another method commonly used to study oscillator chains is to solve the Langevin equations. In this way it is possible to obtain not only numerical but also analytical results in the limit of $N \to \infty$ [15]. Also, analytically exact solutions are possible in the thermodynamic limit for the quantum version of oscillator chain [16, 17].

The Langevin equation is a stochastic differential equation that describes the time evolution of a subset of the degrees of freedom. The original equation was built to describe Brownian motion, given by the collision with the molecules of the fluid with the particle submerged in that very fluid

$$m\frac{d^2\mathbf{x}}{dt^2} = -\lambda\frac{d\mathbf{x}}{dt} + \eta(t) \tag{1.20}$$

where $\mathbf{x}$ and m are the position and the mass of the particle, λ represents the viscous forces and $\eta(t)$ is the noise term describing the effects of the collisions with the molecules of the fluid.

It is actually possible to derive a general Langevin equation from classical mechanics, that is widely used in non equilibrium statistical mechanics: the one in (1.20) is a special case of the general one. In the specific case of oscillator chains in contact at the edges with two reservoirs and with fixed boundary conditions, one has first to consider the Hamiltonian of the system [18]

$$H(x,p) = \sum_{i=1}^{N}\left[\frac{p_i^2}{2m_i} + U(x_i)\right] + \sum_{i=1}^{N}\left[V(x_{i+i} - x_i)\right] \tag{1.21}$$

with V the nearest-neighbour interaction potential and U an external potential (which in our work is not considered). The second step is to add to the equations of motion that derive from the Hamiltonian in (1.21) some additional forces, usually one dissipative and one stochastic term (which is usually a Gaussian white noise), to take into account the interaction of the edges of the chain with the heat baths.

The equations of motion are

$$\dot{p}_1 = f_1 - \frac{\gamma_L}{m_1} p_1 + \eta_L(t) \tag{1.22}$$

$$\dot{p}_i = f_i \text{ for } i = 2...N-1 \tag{1.23}$$

$$\dot{p}_N = f_N - \frac{\gamma_R}{m_N} p_N + \eta_R(t) \tag{1.24}$$

with $f_i = -\frac{\partial H}{\partial x_i}$, $\eta_{N,L}$ the noise terms and $\gamma_{N,L}$ the dissipation coefficients. The solutions of these equations are used to evaluate quantities like the steady-state current and the temperature profile as in the previous section. We are not using this method for various reasons: first, as we have just stated, the Langevin equations are mainly used for the computation of observables, like the current, which are not studied in our work. Secondly, analytical solutions exist exclusively in the thermodynamic limit: we are looking for exact analytical solutions with no approximations.

However we note this method because it is one of the most widespread method used to deal with oscillator chains.

1.4 Our Work

The work of this thesis is focused on the thermodynamic properties of microscopic systems in low dimensions which, as we have explained, are characterized by peculiar features.

In particular we will try to understand how the density and the energy of the particles in a chain change due to the presence of non equilibrium conditions. As we have just illustrated, this kind of system has been studied countless number of times: here we choose a different approach, starting from an idea given in [19] and we deal with the problem in a different way.

More precisely, instead of dealing with the dynamics of the chain and its interaction with the reservoirs, we focus on the heat flux that travels through the chain and that will represent our non equilibrium condition.

This heat flux is taken into account by adding a distortion to the Hamiltonian that describes the oscillator chain.

Even if we share the starting point, we take another path respect to the work in [19], that concerns information theory [20].

We follow instead the steps in [21]: using the distortion of the Hamiltonian as the non equilibrium condition, a harmonic chain with only one fixed edge and where the mass is concentrated on the last particle is studied from three different points of view: analitically, numerically and experimentally. In all the three cases, an amount of energy is detected and it is assumed to be caused by the non equilibrium conditions.

We will build a similar, but not identical, model: in our case a chain of oscillators with fixed edges and equal masses for all particles is used. We try to check if with this new model the energy distortion is actually observed first by trying to get some exact analytical solutions (those in [21] are just obtained with some approximations) and afterwards with some numerical calculations. Here, also the density distortion of particles is taken into account and we check this result by comparing it with the ones obtained in [22] through molecular dynamics.

We are going to consider two different potential energies: the harmonic and the FPU potential, on which we are going to give an overview in the following section.

1.4.1 FPU Potential

The Fermi-Pasta-Ulam potential bears the name of three scientists (Enrico Fermi, John R. Pasta and Stanislaw M. Ulam) that in the 50's decided to test one of the first computers (MANIAC) by solving a theoretical physics problem [23]. It is not commonly known the computer simulation was actually conducted by Mary Tsingou, an American scientist who was working in the MANIAC group as a programmer, hence there were four scientists involved [24].

This was one of the first numerical simulation ever run and that opened the new branch of *numerical experiments*: in fact Fermi had the brilliant idea that computers could be used to study physical problems, not only to perform mere calculation [25].

The aim of their work was to calculate numerically how a crystal reached thermal equilibrium: they considered a chain of particles of unitary mass, linked by a quadratic interaction potential plus a weak nonlinear term. The Hamiltonian of the system was [25]

$$H = \sum_{i=1}^{N} \frac{1}{2} p_i^2 + \sum_{i=1}^{N-1} \left[\frac{1}{2} (q_{i+1} - q_i)^2 + \frac{\alpha}{3} (q_{i+1} - q_i)^3 \right] \tag{1.25}$$

where $q_i = x_i - x_{0i}$ is the displacement from equilibrium of the i-th particle and p_i the momentum.

In normal modes the Hamiltonian is expressed as

$$H = \frac{1}{2} \sum_{k=1}^{N} \left(\dot{\xi}_k^2 + \omega_k^2 \xi_k^2 + \frac{\alpha}{3} \sum_{k,l,m=01}^{N} c_{klm} \xi_k \xi_l \xi_m \omega_k \omega_l \omega_m \right) \tag{1.26}$$

with ξ_i the i-th normal mode (for the whole procedure on normal modes see Appendix A).

What the three scientists thought was that if the energy was concentrated in the first normal mode at the beginning, then after a suitable amount of time

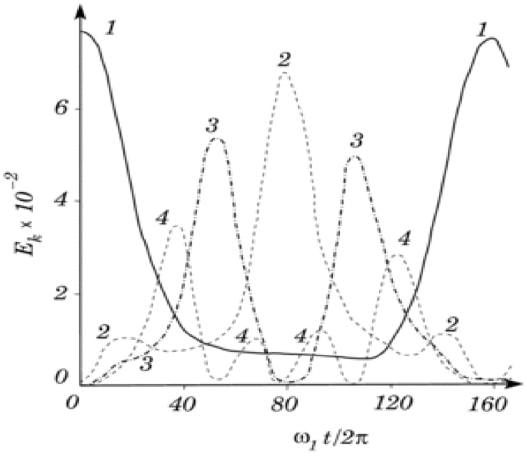


Figure 1.2: Recurrence in FPU model: it is shown how the energy $E_k = \frac{1}{2}\left(\dot{\xi}_k^2 + \omega_k^2 \xi_k^2\right)$ of the first four modes change during time.

it would spread in all the other modes and equipartition would be reached. They were so sure about this result that the simulation was actually run just as a check (as they believed they already knew the behavior of the system). Ironically, what they discovered only by accident was that after remaining in a steady state for a while, the energy was distributed again through the same mode as in their initial conditions. Calculations done years later on more powerful computers showed the same phenomenon.

The explanation of this strange behavior was found ten years later when Zabusky and Kruskal [26] considered the equations of motion of the Hamiltonian in (1.25)

$$\ddot{q}_i = (q_{i+1} + q_{i-1} - 2q_i) + \alpha[(q_{i+1} - q_i) - (q_i q_{i-1})^2] \tag{1.27}$$

and where the concept of solitons was introduced.

It can be actually shown that solitons with sinusoidal initial conditions in a finite system with periodic boundary conditions can go back to their initial conditions.

Here we are not going to discuss this explanation further since we are interested in the shape of the FPU potential: in fact even now models with FPU potential are widely used to describe a wide range of physical systems [27].

In our work we are going to consider this potential as described in [31], where it takes the form

$$V(q) = \frac{1}{2}(q-a)^2 + \frac{\alpha}{3}(q-a)^3 + \frac{\beta}{4}(q-a)^4 \tag{1.28}$$

with q the displacement from equilibrium, a the equilibrium length between 2 particles and α and β the coupling constants. Usually a subversion of (1.28) is generally used where only the cubic or the quartic term is considered: they are called respectively the α and β-FPU model.

We are considering the β-FPU model as in [22] and we are comparing the results. In [22] molecular dynamics is used, and we want to check if our model, even using a complete different procedure, gives the same results and hence is consistent for a chain oscillators with this kind of potential. In an affirmative case we will try to find the analytical solutions of some basic observables of the model, which up to now do not exist.

1.5 A Brief Explanation

We are going to explain briefly what the aim of this work is and why we are studing the model with both harmonic and anharmonic potentials. Beginning with the hamonic one, we know that the solutions for this model already exist not only numerically but also analytically.

We are starting with it to check if our model is consistent: if our results agree with the ones already known in literature then we can have a simpler way to deal with the harmonic chain (since our calculations are easier than the ones in [13]) and, more important, we can extend our model to anharmonic chains by using the FPU potential where exact analytical solutions are still unknown.

Our work is organized as follow: first, we try to build the model with the Hamiltonian distortion given by the heat flux; then we compute some basic observables both analytically and numerically to check if the model is consistent and in agreement with the known results for the harmonic potential. In a positive case we then study the same observables with the FPU potential, also here from both the analytical and numerical point of view, and we try to understand how energy and density of the particles change given the presence of the flux.

A further step to undertake if the model is proved to be successful is to understand if a fluctuation theorem can be applied also in this case. In Appendix C we have illustrated all the fluctuation theorems from the Onsager-Machlup relation to the newest ones from Evans and Searles and Gallavotti and Cohen [28, 29]. This treatment has been done from the analytical point of view and, since it involves ensemble, it is a logical consequence to understand if also with other model which use a modified version of an ensemble, it is possible to extract some fluctuation relations.

PART 1: HARMONIC POTENTIAL

Chapter 2

Theoretical Model

2.1 Basic Idea

As illustrated in the previous chapter, the first step is to build an alternative model that describes a chain of harmonic oscillators in non equilibrium conditions: here we take into account not only the system but also the reservoirs at the edges of the chain.

We can now go deeper in the model and explain the idea on which it is based: instead of considering the dynamics of the system and its interaction with the two reservoirs (as in molecular dynamics or in the Langevin equations), we handle the problem from the Gibb's ensemble point of view [19]. The non equilibrium condition is seen as a distortion of the Hamiltonian as in [21]

$$H \to H + \gamma k_B T J \tag{2.1}$$

where J and T are the ensemble average flux and temperature of the system and γ a Lagrangian multiplier, which means that the non equilibrium conditions are not described by the interaction with the reservoirs, but *by the* *presence of the heat flux* which is generated by this interaction. Hence we focus on the consequence of the non equilibrium condition instead that on the condition (reservoirs) itself.

We have stated in Chapter 1 that in equilibrium a chain of oscillators in contact with a reservoir is described by a canonical ensemble: here, because we are out of equilibrium, we follow the idea in [19] and [21] and we consider a modified ensemble with the Hamiltonian and its distortion.

This means that we set

$$f(x,v) = \frac{e^{-\beta H(x,v) - \gamma J(x,v)}}{\mathcal{K}} \tag{2.2}$$

as the new probability distribution of this 'ensemble' that takes into account the chain and the reservoirs (through the flux) with

$$\mathcal{K} = \int e^{-\beta H(x,v) - \gamma J(x,v)} dxdv \tag{2.3}$$

the new partition function (from now on we are going to drop the quotations on the term ensemble and all the other ones correlated with it since we have fully explained what we mean with these definitions).

In this way, we can use the definition in (1.3) and define the ensemble average of an observables A of the system in the new ensemble as

$$\langle A \rangle = \int A(x,v) f(x,v) dxdv = \frac{\int A(x,v) e^{-\beta H(x,v) - \gamma J(x,v)} dxdv}{\mathcal{K}} \tag{2.4}$$

This formula will be the starting point of all the analytical, and later numerical, calculations.

2.2 Normal Coordinates

2.2.1 Definition of the Hamiltonian

Since in [19] and [21] the Hamiltonian is defined in normal modes we follow the same path and we consider a chain of N particles with the same mass and elastic constant and with fixed edges.

Figure 2.1: Chain of harmonic oscillators with the same mass and elastic constants for all the particles

In this first part, as explained in the introduction, we will deal with a harmonic potential, therefore the Hamiltonian is given by

$$H = T(v_i) + V(x_i) = \frac{1}{2}\sum_{i=0}^{N}\Big[mv_i^2 + k(x_{i+1} - x_i)^2\Big] \tag{2.5}$$

with x_i and v_i the Cartesian coordinates and velocities, and with the following boundary conditions: $x_0 = 0$, $x_{N+1} = x_3 = L$ (the length of the chain), $v_0 = v_3 = \dot{L} = 0$.

If we translate it in normal modes we get (see Appendix A for the whole calculation, where the procedure in [30] has been followed)

$$H = \frac{1}{2}\sum_{i=1}^{N}\Big[\omega_i^2\tilde{x}_i^2 + \tilde{v}_i^2\Big] \tag{2.6}$$

where $\tilde{x}_i$ and $\tilde{v}_i$ are *normal coordinates*, with $\tilde{x}_i = c_i e^{-i\omega_i t}$ and $\tilde{v}_i = \dot{\tilde{x}}_i$ and where ω_i is the frequency associated with the i-th mode.

2.2.2 Definition of the Current

Since for the definition of the Hamiltonian we have used the one in [21], we do the same for the current, hence the global flux is given by

$$J = -\frac{1}{2N} \sum_{i \neq k}^{1,N} j_{ik} (\tilde{x}_i \tilde{v}_k - \tilde{x}_k \tilde{v}_i) = -\frac{1}{N} \sum_{i \neq k}^{1,N} j_{ik} (\tilde{x}_i \tilde{v}_k) \tag{2.7}$$

where N is the number of particles, j_{ik} is the coupling constant between the modes i and k and the last equality is obtained through the invariance under the transformation $\tilde{x}_i \tilde{v}_k \to -\tilde{x}_k \tilde{v}_i$ because $\langle \tilde{x}_i \tilde{v}_k \rangle = \langle \tilde{x}_k \tilde{v}_i \rangle$ [21]. This definition of the flux, which is quite widespread in the literature, we have made is not going to work for this model: this will become clear when we will deal with the computation of the observables of the system in the following paragraph.

2.2.3 Calculation of $\langle x_2 - x_1 \rangle$

The natural step to undertake now is to check the consistency of the model: this is done by computing some basic observables of the system.
For the analytical calculation we are going to use a chain of 2 harmonic oscillators: we start with the quantity $\langle x_2 - x_1 \rangle$, the ensemble average of the distance between the 2 particles, and we try to compute it analytically with the use of the formula (2.4).
For a 2-particle system the Hamiltonian and the global flux are defined as

$$H = \frac{1}{2} \sum_{i=1}^{2} \left[\omega_i^2 \tilde{x}_i^2 + \tilde{v}_i^2 \right] = \left[\omega_1^2 \tilde{x}_1^2 + \omega_2^2 \tilde{x}_2^2 + \tilde{v}_1^2 + \tilde{v}_2^2 \right] \tag{2.8}$$

and

$$J = -\frac{1}{N}\sum_{i\neq k}^{1,2} j_{ik}(\tilde{x}_i\tilde{v}_k) = -\frac{1}{2}\left[j_{12}\tilde{x}_1\tilde{v}_2 + j_{21}\tilde{x}_2\tilde{v}_1\right] \tag{2.9}$$

The quantity we are going to compute is

$$\langle x_2 - x_1\rangle = \frac{\int (x_2 - x_1) e^{-\beta H(\tilde{x},\tilde{v}) - \gamma J(\tilde{x},\tilde{v})} d\tilde{x} d\tilde{v}}{\int e^{-\beta H(\tilde{x},\tilde{v}) - \gamma J(\tilde{x},\tilde{v})} d\tilde{x} d\tilde{v}} \tag{2.10}$$

with $\tilde{x} = (\tilde{x}_1, \tilde{x}_2)$ and $\tilde{v} = (\tilde{v}_1, \tilde{v}_2)$ and, using (2.8) and (2.9), we can rewrite (2.10) as

$$\langle x_2 - x_1\rangle = \frac{\int (x_2 - x_1) e^{-\frac{\beta}{2}[(\omega_1^2\tilde{x}_1^2+\tilde{v}_1^2)+(\omega_2^2\tilde{x}_2^2+\tilde{v}_2^2)]+\frac{\gamma}{2}[j_{12}(\tilde{x}_1\tilde{v}_2)+j_{21}(\tilde{x}_2\tilde{v}_1)]} d\tilde{x} d\tilde{v}}{\int e^{-\frac{\beta}{2}[(\omega_1^2\tilde{x}_1^2+\tilde{v}_1^2)+(\omega_2^2\tilde{x}_2^2+\tilde{v}_2^2)]+\frac{\gamma}{2}[j_{12}(\tilde{x}_1\tilde{v}_2)+j_{21}(\tilde{x}_2\tilde{v}_1)]} d\tilde{x} d\tilde{v}} \tag{2.11}$$

It is really important to underline that while the quantity $\langle x_2 - x_1\rangle$, and consequently $(x_2 - x_1)$ in the integrand, is expressed in *Cartesian coordinates*, all the other variables are expressed in *normal coordinates* (we can see in the notation the presence of the tilde to specify this difference). Therefore we have to express also x_1 and x_2 in normal coordinates

$$x_1 = x_{01} + \eta_1 \tag{2.12}$$

$$x_2 = x_{02} + \eta_2 \tag{2.13}$$

where x_{01} and x_{02} are respectively the equilibrium position of particle 1 and 2, $x_{02} - x_{01} = a$ with a the equilibrium position between the two particles and η_1 and η_2 the displacement from the equilibrium position (see [30] for reference). Following the procedure illustrated in Appendix A, we can use the relations

$$\eta_1 = c_1\frac{1}{\sqrt{2m}}e^{-i\omega_1 t} + c_2\frac{1}{\sqrt{2m}}e^{-i\omega_2 t} \tag{2.14}$$

$$\eta_2 = c_1\frac{1}{\sqrt{2m}}e^{-i\omega_1 t} - c_2\frac{1}{\sqrt{2m}}e^{-i\omega_2 t} \tag{2.15}$$

we obtain

$$\begin{aligned} x_2 - x_1 &= x_{02} + c_1 \frac{1}{\sqrt{2m}} e^{-i\omega_1 t} - c_2 \frac{1}{\sqrt{2m}} e^{-i\omega_2 t} \\ &- x_{01} - c_1 \frac{1}{\sqrt{2m}} e^{-i\omega_1 t} - c_2 \frac{1}{\sqrt{2m}} e^{-i\omega_2 t} \\ &= a - \frac{2c_2}{\sqrt{2m}} e^{-i\omega_2 t} = a - \sqrt{\frac{2}{m}} \tilde{x}_2 \end{aligned} \tag{2.16}$$

The integral in (2.11) becomes

$$\langle x_2 - x_1 \rangle = \frac{\int (a - \sqrt{\frac{2}{m}} \tilde{x}_2) e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v}}{\int e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v}} \tag{2.17}$$

The solution of (2.11) can be obtained without making any explicit calculation. We start with the numerator and we consider the first term in the brackets, whose solution is straightforward

$$\begin{aligned} & \int a e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v} \\ = & \; a \int e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v} \\ = & \; a\mathcal{K} \end{aligned} \tag{2.18}$$

with $\mathcal{K}$ partition function.

We can go on with the second term in the brackets

$$\begin{aligned} & \int -\sqrt{\frac{2}{m}} \tilde{x}_2 e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v} \\ & -\sqrt{\frac{2}{m}} \int \tilde{x}_2 e^{-\frac{\beta}{2}[(\omega_1^2 \tilde{x}_1^2 + \tilde{v}_1^2) + (\omega_2^2 \tilde{x}_2^2 + \tilde{v}_2^2)] + \frac{\gamma}{2}[j_{12}(\tilde{x}_1 \tilde{v}_2) + j_{21}(\tilde{x}_2 \tilde{v}_1)]} d\tilde{x} d\tilde{v} \end{aligned} \tag{2.19}$$

also here we do not need any calculation: the result in (2.19) is zero, because we are integrating a function, $\tilde{x}_2$ times all the quadratic exponential terms, that is odd in a symmetric domain (from $-\infty$ to $+\infty$).

The solution of (2.10) is then

$$\langle x_2 - x_1 \rangle = \frac{a\mathcal{K}}{\mathcal{K}} = a \tag{2.20}$$

which, as we have said before, corresponds to the equilibrium position between particles 1 and 2.

In conclusion there is no trace of the distortion in the computed observable, no matter the number of particles: this is not only the opposite of what we would have expected from a theoretical point of view (since *there is* a distortion and we should be able to see its effects) but also from what we know from the experiments [21].
Anyway, this is not in contrast with the work in [19] and [21] for two reasons: first of all, as we have stressed in the introduction, the properties of the chain are strongly dependent on the boundary conditions and ours are different from the ones in [19] and [21]. Secondly, in the two papers only quadratic observables are taken into account while we are also interested in the linear ones and the problem we have just illustrated arises with these last kind of observables.

To solve this *impasse* two paths are feasible: either we change the definition of the flux or we consider a new whole ensemble (to which a distortion will be added later). We choose to first path because in the previous work, starting with a modified canonical ensemble has given primising results, so it seems quite reasonable to persist on this route.
Also, the microscopical definition of the flux is not univocal and the question of whether or not it is possible to find one that is suitable for all physical systems is still an open problem.

2.3 Cartesian Coordinates and Velocities

2.3.1 Definition of the Hamiltonian

Since we have decided to use a different definition of the current, we express now the Hamiltonian in Cartesian coordinates: the only reason to use the normal ones was to compare our results more easily with the ones in [19] and [21], but now this direct comparison is not possible anymore. Hence, we have decided to use the Cartesian coordinates so that there is no need to pass from one coordinate to the other, simplifying the calculation.

In Cartesian coordinates, the Hamiltonian for a 2-particle system is written as

$$\begin{aligned} H &= \frac{1}{2}\sum_{i=0}^{2}\left[mv_i^2 + k(x_{i+1}-x_i)^2\right] \\ &= \left[\frac{m}{2}v_1^2 + \frac{m}{2}v_2^2 + kx_1^2 + kx_2^2 - kx_1x_2 + \frac{1}{2}kL^2\right] \qquad (2.21) \end{aligned}$$

with the following boundary conditions $x_0 = 0$, $x_3 = L$ (L is the length of the chain) and $v_0 = v_3 = \dot{L} = 0$ and with the same properties as before: fixed edges, same value of the mass and the elastic constant for all particles.

2.3.2 Definition of the Current

We have ruled out the definitions for the flux in [19] and [21], because here the fluxes are both described by using only quadratic variables and we would have the problem observed in the previous section for linear observables.
Since we have written the Hamiltonian in Cartesian coordinates, we have to do the same with the flux.
We have followed the formula used in [31] and [18] where an extensive treatement of chain of oscillators is illustrated.

In particular we focus on the definition for the flux in [31] in which a chain of oscillators is described by

$$H = \sum_{i}^{N} \left[\frac{p_i^2}{2m_i} + U(x_i) + V(x_{i+1} - x_i) \right] \tag{2.22}$$

Here also the mass and the coupling constant are the same for all particles (which is suitable with our case), $V(x_{i+1} - x_i)$ is the interaction potential between two particles, which is not explicitly specified here and, along with our case, will be a harmonic or a FPU potential, and $U(x_i)$ is the on site potential of the particle i.

In [31], a continuity equation is used to get the microscopic definition of the flux: we will do the same, except that in our case $U(x_i) = 0$.

In a one-dimensional fluid or in solid, the heat flux is stated to coincide with the energy flux, so we can write the continuity equation as

$$\frac{dh(x,t)}{dt} + \frac{\partial j(x,t)}{\partial x} = 0 \tag{2.23}$$

with $j(x,t)$ the energy current density and $h(x,t)$ the energy density, which can be written as the sum of the contributions of the particles, each one located in the instantaneous position x

$$h = \sum_i h_i \delta(x - x_i) \tag{2.24}$$

and with h_i, the microscopic energy density, defined as

$$h_i = \frac{p_i^2}{2m_i} + \frac{1}{2} \left[V(x_{i+1} - x_i) + V(x_i - x_{i-1}) \right] \tag{2.25}$$

Also the flux is defined as the sum of local contributions

$$j(x,t) = \sum_i j_i \delta(x - x_i) \tag{2.26}$$

We are looking for the local definition of the flux j_i. If we time-derive h_i we obtain

$$\frac{dh_i}{dt} = m_i \dot{x}_i \ddot{x}_i - \frac{1}{2} \left[(x_{i+1} - x_i) F(x_{i+1} - x_i) + (x_i - x_{i-1}) F(x_i - x_{i-1}) \right] \tag{2.27}$$

since the equations of motion are

$$m_i \ddot{x}_i = -F(x_{i+1} - x_i) + F(x_i - x_{i-1}) \tag{2.28}$$

we can substitute (2.28) in (2.27), which brings to

$$\frac{dh_i}{dt} = -\frac{1}{2}\left[(\dot{x}_{i+1} + \dot{x}_i)F(x_{i+1} - x_i) - (\dot{x}_i + \dot{x}_{i-1})F(x_i - x_{i-1})\right] \tag{2.29}$$

that we can write as

$$\frac{dh_i}{dt} + \frac{j_i - j_{i-1}}{a} = 0 \tag{2.30}$$

with j_i the microscopic flux defined as

$$j_i = -\frac{1}{2}a(\dot{x}_{i+1} + \dot{x}_i)F(x_{i+1} - x_i) \tag{2.31}$$

with $F(x_{i+1} - x_i) = -\frac{\partial V}{\partial x_i}$ and a the equilibrium distance between two particles.

This definition of the flux raises no problem for this model: all the analytical computations done to show this statement will be illustrated in the next section.

Chapter 3

Analytical Results

3.1 Introduction

In the previous chapter we have found a definition of the current that can be suitable for our model, hence the aim is now to check if our description of the system is consistent with this definition.

For this reason we first try to compute some basic properties of the chain, to understand if it is possible to obtain exact analytical solutions for the observables that characterize the system.

As before, we start by considering a chain of $N = 2$ harmonic oscillators: if the problem is analytically solved we can extend the calculation to a larger number of particles.

In the chain, masses and elastic couplings are equal for all particles and edges are fixed. In equilibrium conditions the Hamiltonian is given by

$$H = T(v_i) + V(x_i) = \frac{1}{2} \sum_{i=0}^{2} \Big[m v_i^2 + k(x_{i+1} - x_i)^2 \Big] \tag{3.1}$$

with x_i and v_i the Cartesian coordinates and velocities, and with the following boundary conditions: $x_0 = 0$, $x_{N+1} = x_3 = L$ (the length of the chain),

$v_0 = v_3 = \dot{L} = 0$.

For $N = 2$ particles the Hamiltonian is explicitly defined as in (2.21)

$$H = \left[k \left(x_1^2 + x_2^2 - x_1 x_2 + \frac{L^2}{2} \right) + \frac{m}{2} \left(v_1^2 + v_2^2 \right) \right] \tag{3.2}$$

As explained before, non equilibrium conditions are now given by a correction to the Hamiltonian: the global flux, for the 2-particle case, is the sum of the following microscopic fluxes (see (2.26))

$$J = \sum_{i=0}^{2} = j_0 + j_1 + j_2 \tag{3.3}$$

with, following the definition in (2.31) and with $F(x_{i+1} - x_i) = -k(x_{i+1} - x_i)$,

$$j_0 = -\frac{ka}{2} (x_1 v_1)$$

$$j_1 = -\frac{ka}{2} (v_2 x_2 - x_1 v_2 + x_2 v_1 - x_1 v_1)$$

$$j_2 = -\frac{ka}{2} (L v_2 - x_2 v_2)$$

The global flux in (3.3) explicitly becomes

$$J = -\frac{ka}{2} (v_1 x_2 - x_1 v_2 + L v_2) \tag{3.4}$$

3.2 Calculation of $\langle x_2 - x_1 \rangle$

We start by computing the ensemble average of the distance between the two particles, which is defined as

$$\langle x_2 - x_1 \rangle = \frac{\int (x_2 - x_1) e^{-\beta H(x,v) - \gamma J(x,v)} dx dv}{\mathcal{K}} \tag{3.5}$$

with H and J given explicitly by (3.2) and (3.4), $x = (x_1, x_2)$ and $v = (v_1, v_2)$ the phase space coordinates and $\mathcal{K}$ the partition function in the modified ensemble, so that the whole integral is

$$\langle x_2 - x_1\rangle = \frac{\int (x_2 - x_1) e^{-\beta k\left(x_1^2+x_2^2-x_1x_2+\frac{L^2}{2}\right)-\frac{\beta m}{2}\left(\dot{x}_1^2+\dot{x}_2^2\right)+\frac{\gamma k a}{2}\left(\dot{x}_1x_2-x_1\dot{x}_2+L\dot{x}_2\right)} dxdv}{\int e^{-\beta k\left(x_1^2+x_2^2-x_1x_2+\frac{L^2}{2}\right)-\frac{\beta m}{2}\left(\dot{x}_1^2+\dot{x}_2^2\right)+\frac{\gamma k a}{2}\left(\dot{x}_1x_2-x_1\dot{x}_2+L\dot{x}_2\right)} dxdv} \tag{3.6}$$

We illustrate the full procedure for the computation of the integral in (3.6) for completeness: it will be the same for all the following integrals.
We start by computing the partition function in the denominator: we first integrate the variable v_1 and v_2 so we consider all the terms in the denominator in (3.6) that depends on this variable

$$\int e^{-\frac{\beta m}{2}v_1^2+\frac{\gamma k a}{2}v_1x_2} dv_1 = \frac{\sqrt{2\pi}}{\sqrt{\beta m}} e^{\frac{a^2\gamma^2k^2}{8\beta m}x_2^2} \tag{3.7}$$

$$\int e^{-\frac{\beta m}{2}v_2^2-\frac{\gamma k a}{2}x_1v_2+\frac{\gamma k a}{2}Lv_2} dv_2 = \frac{\sqrt{2\pi}}{\sqrt{\beta m}} e^{\frac{a^2\gamma^2k^2}{8\beta m}L^2+\frac{a^2\gamma^2k^2}{8\beta m}x_1^2-\frac{a^2\gamma^2k^2}{4\beta m}Lx_1} \tag{3.8}$$

We can go on with this procedure and integrate the remaining variables x_1 and x_2. Which means

$$\int e^{-\beta k x_1^2+\beta k x_1 x_2+\frac{a^2\gamma^2k^2}{8\beta m}x_1^2-\frac{a^2\gamma^2k^2}{4\beta m}Lx_1} dx_1 = \tag{3.9}$$

$$\sqrt{\frac{8\pi\beta m}{-8\beta^2 k m + a^2k^2\gamma^2}} e^{-\frac{k^4a^4\gamma^4L^2}{k^2a^2\gamma^2-8\beta^2mk}-\frac{2\beta^3mk^2x_2^2}{k^2a^2\gamma^2-8\beta^2mk}+\frac{\beta k^3a^2\gamma^2Lx_2}{k^2a^2\gamma^2-8\beta^2mk}} \tag{3.10}$$

and for the last variable x_2

$$\int e^{-\beta k x_2^2+\beta k L x_2+\frac{k^2a^2\gamma^2x_2^2}{8\beta m}-\frac{2\beta^3mk^2x_2^2}{k^2a^2\gamma^2-8\beta^2mk}=+\frac{\beta k^3a^2\gamma^2L}{k^2a^2\gamma^2-8\beta^2mk}} dx_2 = \tag{3.11}$$

$$\frac{\sqrt{\pi}\sqrt{8\beta m(8\beta^2 mk - k^2a^2\gamma^2)}}{\sqrt{48\beta^4m^2k^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4}} e^{-\frac{16\beta^2m^2(-8\beta^3mk^2L+2\beta k^3a^2\gamma^2)^2}{(48\beta^4m^2k^2-16\beta^2mk^3a^2\gamma^2+k^4a^4\gamma^4)^2}} \tag{3.12}$$

In conclusion the result for the partition function is

$$\mathcal{K} = \frac{16\pi^3}{\sqrt{48\beta^4m^2k^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4}} \times \tag{3.13}$$

$$e^{-\frac{\beta kL^2}{2} + \frac{k^2a^2\gamma^2L^2}{8\beta m} - \frac{k^4a^4\gamma^4L^2}{k^2a^2\gamma^2-8\beta^2mk} - \frac{16\beta^2m^2(-8\beta^3mk^2L+2\beta k^3a^2\gamma^2)^2}{(48\beta^4m^2k^2-16\beta^2mk^3a^2\gamma^2+k^4a^4\gamma^4)^2}} \tag{3.14}$$

Following the same procedure we can integrate also the numerator and considering the following integrals

$$\int x_1 e^{-\beta H(x,v)-\gamma J(x,v)}dxdv \quad \text{and} \quad \int x_2 e^{-\beta H(x,v)-\gamma J(x,v)}dxdv \tag{3.15}$$

and putting everything together, the final results are

$$\langle x_1 \rangle = \frac{16\beta^4m^2k^2L - 8\beta^2mk^3a^2\gamma^2L + k^4a^4\gamma^4L}{48\beta^4m^2k^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4} \tag{3.16}$$

$$\langle x_2 \rangle = \frac{32\beta^4m^2k^2L - 8\beta^2mk^3a^2\gamma^2L}{48\beta^4m^2k^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4} \tag{3.17}$$

which brings to

$$\langle x_2 - x_1 \rangle = \frac{16\beta^4m^2k^2L - k^4a^4\gamma^4L}{48\beta^4m^2k^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4} \tag{3.18}$$

To obtain these results, the following constraints have to be observed

$$\begin{cases} -\beta m < 0 \\ -\beta k + \dfrac{k^2a^2\gamma^2}{8\beta m} < 0 \\ \dfrac{48\beta^4k^2m^2 - 16\beta^2mk^3a^2\gamma^2 + k^4a^4\gamma^4}{8\beta m(k^2a^2\gamma^2 - 8\beta^2mk)} < 0 \end{cases}$$

The first inequality is always satified, because β and m are always positive. After some manipulations and decomposition of the numerator in the third inequality the system becomes

$$\begin{cases} 8\beta^2 m > ka^2\gamma^2 \\ \dfrac{(k^2a^2\gamma^2 - 4\beta^2 mk)(k^2a^2\gamma^2 - 12\beta^2 mk)}{8\beta m(k^2a^2\gamma^2 - 8\beta^2 mk)} < 0 \end{cases}$$

and with some calculation in the second inequality

$$\begin{cases} 8\beta^2 m > ka^2\gamma^2 \\ 4\beta^2 m > ka^2\gamma^2 \;\vee\; 8\beta^2 m > ka^2\gamma^2 > 12\beta^2 m \end{cases}$$

which brings to the following solution for our system

$$4\beta^2 m > ka^2\gamma^2 \tag{3.19}$$

We can get some qualitative considerations in (3.19) by putting $a = 1$, which is a usual routine for oscillator chains, and by putting also $k = m = 1$: this is done because we are dealing with systems where the mass and the coupling constant have the same weight in the dynamics since our first aim is to understand the relation between the Hamiltonian and its distortion.
In this way, the inequality becomes

$$4\beta^2 > \gamma^2 \tag{3.20}$$

which in the end gives

$$2\beta > \gamma \tag{3.21}$$

This means that the contribution of the current to the ensemble cannot be preponderant with respec to the contribution of the energy of the chain in equilibrium.

It is also important to stress that this inequalities proved to be quite easy to solve only because all the constants are positive by definition.

3.3 Calculation of $\langle x_1^2 \rangle$ and $\langle x_2^2 \rangle$

As a second step we calculate the second momentum of the variable x_1 and x_2, whose results are

$$\begin{aligned}
\langle x_1^2 \rangle \; = \; & (256\beta^8 m^4 k^4 L^2 + 1536\beta^7 m^4 k^3 - 256\beta^6 m^3 k^5 a^2 \gamma^2 L^2 - 704\beta^5 m^3 k^4 a^2 \gamma^2 \\
& +96\beta^4 m^2 k^6 a^4 \gamma^4 L^2 + 96\beta^3 m^2 k^5 a^4 \gamma^4 - 16\beta^2 m k^7 a^6 \gamma^6 L^2 - 4\beta m k^6 a^6 \gamma^6 \\
& +k^8 a^8 \gamma^8 L^2)/ \\
& (2304\beta^8 m^4 k^4 - 1536\beta^6 m^3 k^5 a^2 \gamma^2 + 352\beta^4 m^2 k^6 a^4 \gamma^4 - 32\beta^2 m k^7 a^6 \gamma^6 + \\
& k^8 a^8 \gamma^8) \qquad (3.22)
\end{aligned}$$

$$\begin{aligned}
\langle x_2^2 \rangle \; = \; & (1024\beta^8 m^4 k^4 L^2 + 1536\beta^7 m^4 k^3 - 512\beta^6 m^3 k^5 a^2 \gamma^2 L^2 - 702\beta^5 m^3 k^4 a^2 \gamma^2 \\
& +64\beta^4 m^2 k^6 a^4 \gamma^4 L^2 + 96\beta^3 m^2 k^5 a^4 \gamma^4 - 4\beta m k^6 a^6 \gamma^6)/ \\
& (2304\beta^8 m^4 k^4 - 1536\beta^6 m^3 k^5 a^2 \gamma^2 + 352\beta^4 m^2 k^6 a^4 \gamma^4 - 32\beta^2 m k^7 a^6 \gamma^6 \\
& +k^8 a^8 \gamma^8) \qquad (3.23)
\end{aligned}$$

where the calculations lead to the same constraints on the parameter space as before.

We are actually more interested in the variance of this observables since our first aim was to understand if the presence of a heat flux leads to an energy distortion. The results are the following

$$\begin{aligned}\langle x_1^2\rangle - \langle x_1\rangle^2 = \langle x_2^2\rangle - \langle x_2\rangle^2 \;=\;& (1536\beta^7 m^4 k^3 - 704\beta^5 m^3 k^4 a^2\gamma^2 \\ & +96\beta^3 m^2 k^5 a^4\gamma^4 - 4\beta m k^6 a^6\gamma^6)/ \\ & (2304\beta^8 m^4 k^4 - 1536\beta^6 m^3 k^5 a^2\gamma^2 \\ & +352\beta^4 m^2 k^6 a^4\gamma^4 - 32\beta^2 m k^7 a^6\gamma^6 \\ & +k^8 a^8\gamma^8) \qquad (3.24)\end{aligned}$$

It is straightforward to notice that the variance is the same for the two particles.

3.4 Calculation of $\langle v_2 - v_1 \rangle$

After considering the spatial coordinates, we can now focus on the velocities of the two particles

$$\langle v_1\rangle = \langle v_2\rangle = \frac{48\beta^3 mka\gamma L - 12\beta k^2 a^3\gamma^3 L}{144\beta^4 m^2 - 48\beta^2 mka^2\gamma^2 + 3k^2a^4\gamma^4} \qquad (3.25)$$

as expected this observable is the same for both particles.

For these results, we have the following constraints

$$\begin{cases} -\dfrac{\beta m}{2} + \dfrac{ka^2\gamma^2}{12\beta} < 0 \\ \dfrac{48\beta^4 m^2 - 16\beta^2 mka^2\gamma^2 + k^2a^4\gamma^4}{16\beta(ka^2\gamma^2 - 6\beta^2 m)} < 0 \end{cases}$$

which, after some manipulations, leads to

$$\begin{cases} 6\beta^2 m > ka^2\gamma^2 \\ \dfrac{(ka^2\gamma^2 - 4\beta^2 m)(ka^2\gamma^2 - 12\beta^2 m)}{16\beta(ka^2\gamma^2 - 6\beta^2 m)} < 0 \end{cases}$$

After some calculation in the second inequality we have

$$\begin{cases} 6\beta^2 m > ka^2\gamma^2 \\ 4\beta^2 m > ka^2\gamma^2 \ \vee \ 6\beta^2 m > ka^2\gamma^2 > 12\beta^2 m \end{cases}$$

which brings to the following solution for our system

$$4\beta^2 m > a^2\gamma^2 k \tag{3.26}$$

the same as in (3.19).

3.5 Calculation of $\langle v_1^2 \rangle$ and $\langle v_2^2 \rangle$

The second momentum of v_1 and v_2 is

$$\begin{aligned} \langle v_1^2 \rangle = \langle v_2^2 \rangle \;=\; & (20736\beta^7 m^3 + 2304\beta^6 m^2 k^2 a^2 \gamma^2 L^2 - 10368\beta^5 m^2 k a^2 \gamma^2 \\ & -1152\beta^4 m k^3 a^4 \gamma^4 L^2 + 1584\beta^3 m k^2 a^4 \gamma^4 + 144\beta^2 k^4 a^6 \gamma^6 L^2 \\ & -72\beta k^3 a^6 \gamma^6)/ \\ & (20736\beta^8 m^4 - 13824\beta^6 m^3 k a^2 \gamma^2 + 3168\beta^4 m^2 k^2 a^4 \gamma^4 \\ & -288\beta^2 m k^3 a^6 \gamma^6 + 9k^4 a^8 \gamma^8) \end{aligned} \tag{3.27}$$

while the variance is given by

$$\begin{aligned} \langle v_1^2 \rangle - \langle v_1 \rangle^2 = \langle v_2^2 \rangle - \langle v_2 \rangle^2 \;=\; & (20736\beta^7 m^3 - 10368\beta^5 m^2 k a^2 \gamma^2 \\ & +1584\beta^3 m k^2 a^4 \gamma^4 - 72\beta k^3 a^6 \gamma^6)/ \\ & (20736\beta^8 m^4 k^4 - 13824\beta^6 m^3 k a^2 \gamma^2 \\ & +3168\beta^4 m^2 k^2 a^4 \gamma^4 - 288\beta^2 m k^3 a^6 \gamma^6 \\ & +9k^4 a^8 \gamma^8) \end{aligned} \tag{3.28}$$

Also here, the costraints we have to observe in the parameter space are the same as before.

3.6 Conclusions

In conclusion we have just shown that the observable can be defined analytically for a 2-particle system and with the definition of Hamiltonian in (3.1) and of the flux in (2.31): anyway this is possible only with some constraints in the parameter space, which are the same for all the observables (3.19) and reduce to (3.21) if the constants are all set to 1.

One can notice that, since we are focused on the correlation between H and J, which means between β and γ that are the physical parameters of the model representing the system and its distortion, this inequality can be seen as an *upper limit* for γ, that cannot be higher than a certain value represented by $\beta = 1/k_B T$ with T the temperature of the chain in equilibrium.

Finally, it is important to underline that for $\gamma = 0$, we obtain the same value as the ones in equilibrium condition (as we would have expected).

Chapter 4

Numerical Results

4.1 Monte Carlo Simulation

After dealing with the analytical calculation and the theoretical model is fixed, the following step is to investigate if and how the properties of the system change for a large number of particles: to answer this question, a Monte Carlo simulation is needed [32].

Our aim is to study the behavior of a $N = 50$ particle system through the computation of the same observables of the previous chapter.

For the numerical computation a basic Monte Carlo formula for the resolution of integrals is used [33, 34].

If one wants to compute the quantity

$$I = \int_a^b f(\xi) d\xi \tag{4.1}$$

without actually solving the integral, meaning without finding the primitive of the integrand $f(\xi)$, a simple formula can be used. In fact it is possible to evaluate the function $f(\xi)$ for $\mathcal{N}$ times, where each time ξ is a random number from a uniform distribution in the interval $[0, 1]$ which can be extended to the generic interval $[a, b]$.

In this way the value of the integral is obtained through the formula

$$I = \frac{\sum_{i=1}^{\mathcal{N}} f(\xi_i)}{\mathcal{N}} \tag{4.2}$$

that is, by getting the average of $f(\xi)$ over $\mathcal{N}$, the number of times the value $f(\xi)$ is estimated.

Of course it is possible with some manipulation to consider different kinds of distributions instead of the uniform one and to extend the formula to multiple dimensions by considering random vectors instead of random numbers.

For example, in statistical mechanics one usually has to deal with the computation of the ensemble average of the observables.

For the canonical ensemble we have seen that (1.3)

$$\langle A \rangle = \frac{\int A(\xi) e^{-\beta H(\xi)} d\xi}{Z} \tag{4.3}$$

with $\xi = (x, v)$ represents the spatial and momentum coordinates in the phase space and Z is the partition function.

In this case, if we want to apply the same formula as in (4.2) we need to evaluate the observable $A(\xi)$ number of times $\mathcal{N}$, where ξ is now a random vector of dimension $2N$, because our model is one-dimensional, given by the distribution

$$\rho(\xi)_{EQ} = \frac{e^{-\beta H(\xi)}}{Z} \tag{4.4}$$

which is obviously a Gaussian distribution.

In our model, because of the presence of the flux, the quantity in the exponential has an additional term, and the ensemble average of the observable is

$$\langle A \rangle = \frac{\int A(\xi) e^{-\beta H(\xi) - \gamma J(\xi)} d\xi}{\mathcal{K}} \tag{4.5}$$

The only difference with respect to the equilibrium case is the distribution for the randon vector ξ, which is now

$$\rho(\xi) = \frac{e^{-\beta H(\xi) - \gamma J(\xi)}}{\mathcal{K}} \tag{4.6}$$

with

$$\mathcal{K} = \int e^{-\beta H(\xi) - \gamma J(\xi)} d\xi \tag{4.7}$$

and that should be a multivariate Gaussian distribution in order to create the $\mathcal{N}$ random vectors ξ. That means it should have the form

$$\rho(\xi)_{GAUSS} = \frac{1}{(2\pi)^{k/2} |\Sigma|^{\frac{1}{2}}} e^{-\frac{1}{2}(\xi-\mu)^T \Sigma^{-1} (\xi-\mu)} \tag{4.8}$$

with Σ the covariance matrix and μ the average of the distribution.
Which values should Σ and μ have to reproduce (4.6)?
To answer this question, we should solve the following equation

$$-\frac{1}{2}(\xi-\mu)^T \Sigma^{-1} (\xi-\mu) = -\beta H(\xi) - \gamma J(\xi) \tag{4.9}$$

We can make some manipulation on the left hand side of (4.9) which brings to

$$\begin{aligned} -\frac{1}{2}(\xi-\mu)^T \Sigma^{-1} (\xi-\mu) &= -\frac{1}{2}\left(\xi^T \Sigma^{-1} \xi - \xi^T \Sigma^{-1} \mu - \mu^T \Sigma^{-1} \xi + \mu^T \Sigma^{-1} \mu\right) \\ &= -\frac{1}{2}\left(\xi^T \Sigma^{-1} \xi - 2\xi^T \Sigma^{-1} \mu + \mu^T \Sigma^{-1} \mu\right) \end{aligned} \tag{4.10}$$

Now we can solve (4.9) by considering the linear and the quadratic terms separately (the constant term will be ruled out by the normalization). We put all the quadratic terms of the right hand side of (4.9) equal to first term

in the parenthesis in (4.10) and the linear terms equal to the second one.
By solving these two equations we get the values of Σ and μ that reproduce the probability distribution in (4.6) and we can get $\mathcal{N}$ times the random vector ξ. By applying the formula in (4.2), we can then compute (4.5).

4.2 The Idea Behind Code

We now try to give a few insights on the code used to compute quantities such as (4.5) using the Monte Carlo method explained in the previous section.
First of all we have to build the covariance matrix Σ and the average μ to get the probability distribution $f(\xi)$ of the random vectors ξ.
Our code runs in this way: we first construct a matrix with the quadratic terms of $-\beta H(\xi) - \gamma J(\xi)$ for a certain number of particles (in our case it will be $N = 50$) and we get the matrix Σ^{-1}.
Since we need to put the value of the covariance matrix Σ in the Monte Carlo simulation, with the second code we get the inverse of Σ^{-1}. Afterwards we get the average μ by comparing the linear terms in (4.9). Finally, when we have all the values we need for the probability distribution we can run the last code by using Σ and μ and compute the observables of the system we are studing.
The complete codes used to run the simulations are illustrated in Appendix B.

4.3 2-Particle System

The first step has been to run our code for a $N = 2$ particle system, to check if the results were the same both analytically and numerically. We have made different tests in which the values of the parameters have been changed to be sure to have a strong correspondence between the analytical and numerical results for a wide range of the parameter space.

As it is shown in the charts the agreement between the results is quite satisfactory. In the first column there are the analytical results, while in the second one the numerical data which have been cut off to the decimal digit in which we have uncertainty due to statistical error.

Observable	Analytical Result	Numerical Result ± Standard Deviation
$\langle x_1 \rangle$	0.818181813	$0.819 \pm 1 \cdot 10^{-3}$
$\langle x_2 \rangle$	2.18181801	$2.182 \pm 1 \cdot 10^{-3}$
$\langle x_1^2 \rangle$	1.51790631	$1.517 \pm 2 \cdot 10^{-3}$
$\langle x_2^2 \rangle$	5.60881519	$5.611 \pm 4 \cdot 10^{-3}$
$\langle v_1 \rangle = \langle v_2 \rangle$	1.09090912	$1.090 \pm 1 \cdot 10^{-3}$
$\langle v_1^2 \rangle = \langle v_2^2 \rangle$	2.40220404	$2.401 \pm 3 \cdot 10^{-3}$

Table 4.1: $\beta = \gamma = m = k = a = 1$

Observable	Analytical Result	Numerical Result ± Standard Deviation
$\langle x_1 \rangle$	0.973614812	$0.974 \pm 1 \cdot 10^{-3}$
$\langle x_2 \rangle$	2.02638507	$2.027 \pm 1 \cdot 10^{-3}$
$\langle x_1^2 \rangle$	2.32630682	$2.325 \pm 2 \cdot 10^{-3}$
$\langle x_2^2 \rangle$	5.48461819	$5.487 \pm 4 \cdot 10^{-3}$
$\langle v_1 \rangle = \langle v_2 \rangle$	0.316622674	$0.317 \pm 1 \cdot 10^{-3}$
$\langle v_1^2 \rangle = \langle v_2^2 \rangle$	1.38390183	$1.383 \pm 2 \cdot 10^{-3}$

Table 4.2: $\beta = a = 1$, $m = 0.8$ and $\gamma = k = 0.5$

Observable	Analytical Result	Numerical Result ± Standard Deviation
$\langle x_1 \rangle$	0.473684311	$0.475 \pm 2 \cdot 10^{-3}$
$\langle x_2 \rangle$	2.52631617	$2.528 \pm 2 \cdot 10^{-3}$
$\langle x_1^2 \rangle$	2.63666081	$2.633 \pm 4 \cdot 10^{-3}$
$\langle x_2^2 \rangle$	8.79455376	$8.798 \pm 9 \cdot 10^{-3}$
$\langle v_1 \rangle = \langle v_2 \rangle$	2.52631593	$2.527 \pm 2 \cdot 10^{-3}$
$\langle v_1^2 \rangle = \langle v_2^2 \rangle$	11.2945518	$11.29 \pm 1 \cdot 10^{-2}$

Table 4.3: $\gamma = a = 1$, $\beta = k = 0.8$ and $m = 0.5$

4.4 50-Particle System

Since we know that with our model for a 2-particle system it is possible to obtain analytical results that are in agreement with the ones from the Monte Carlo simulations we can now consider a larger number of particles and run our code for a 50-particle system. Here, as before, we are computing some basic observable of our oscillator chain for different values of γ (hence for different values of the distortion).

The aim of this part of the work is to understand, first, if our results are in agreement with the ones already known for harmonic oscillator chains, and, secondly, how the observables are affected by non equilibrium conditions and if it is actually possible to see a distortion with respect to the equilibrium case.

One of the most important result of this section is the computation of the kinetic energy $\langle p_i^2 \rangle$. For system out of equilibrium we have the relation $\langle p_i^2 \rangle = T_i$ defines the kinetic temperature T_i [13].
It is important to stress that we use the term *kinetic temperature* because it is impossible in this condition to define the temperature as in the classic mechanic statistical case, where it is based on the canonical distribution with respect to the energy of the whole system (see [14] for a full explanation).
What we can observe in figure (4.1) is that the kinetic temperature has a constant behavior (with the exception of the particles at the boundaries), with a shift depending on the strength of the distortion, the same that was observed in [13] (see Fig.(4.2)) and that was the most important result on the paper.
We want to stress the fact that up to now the agreement between the two results is only *qualitative*: in fact we are considering different values of the distortion (which is not done in [13]), so we are just focused on the general behavior of the observable.
The same results are obtained in [22] (see Fig.(4.3)), where the chain is also harmonic, however they are obtained through molecular dynamics simulations. In the paper, since the equations of motion are considered, the results are obtained for different values of the intensity of the interaction between the chain and the reservoirs: as in our case there is a shift for these different values but the temperature profile is always constant. That means that our model with the harmonic potential is in agreement, for this observable, with both analytical and numerical solutions already known in literature.

Also another important quantity, the variance of $\langle x \rangle$, which is defined

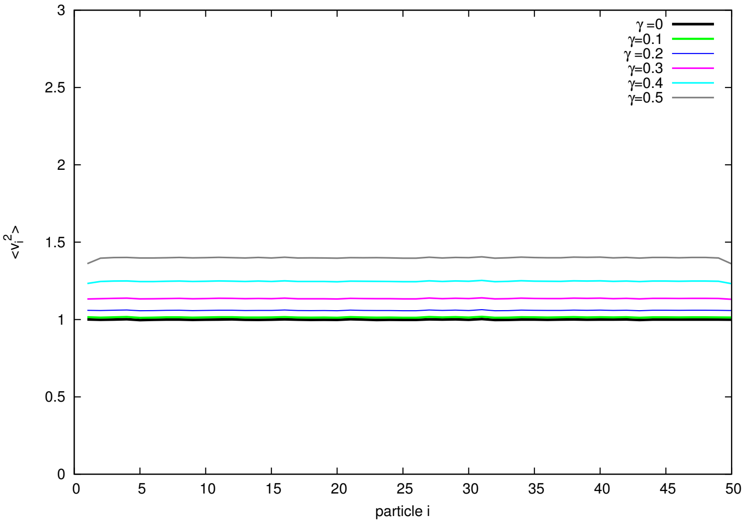


Figure 4.1: Ensemble Average of the Kinetic Energy of the i particle for different values of γ

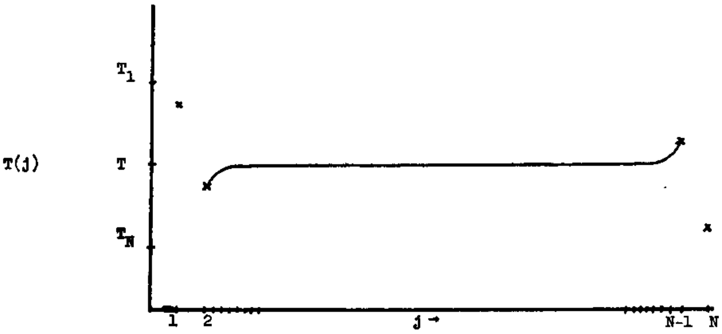


Figure 4.2: Kinetic Temperature of the j particle from [13] (reproduced with the permission of *Journal of Mathematical Physics*)

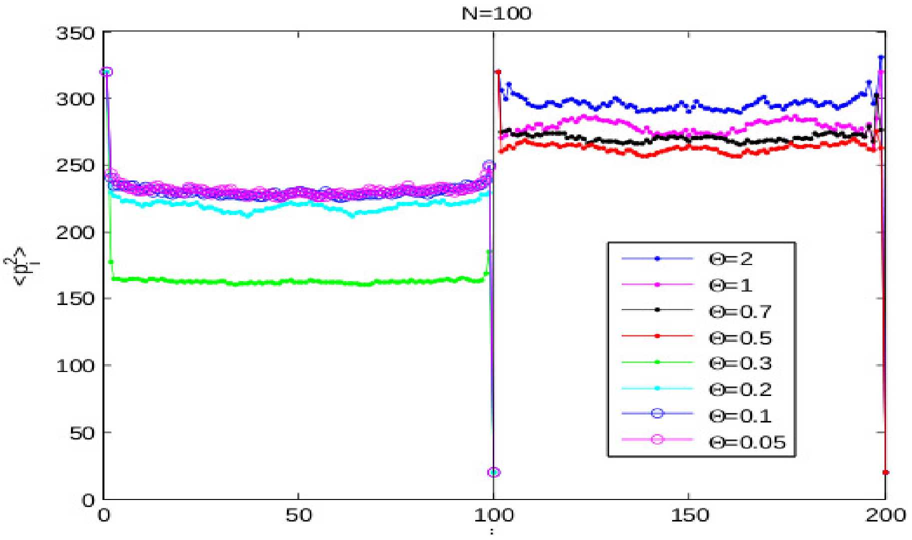


Figure 4.3: Temperature Profile of a 100-particle system in [22] for different values of θ, which represents the strength of the interaction between the chain and the reservoirs (reproduced with the permission of *Phys. Rev. E*)

as $\langle x^2 \rangle - \langle x \rangle^2$, has been taken into account to compare it with the results obtained in [21].

It is commonly known that the variance of the position is connected to the energy: in fact the larger the amplitude of oscillations, the greater the required energy. Also, thanks to the virial theorem, the kinetic energy is connected in turn to the potential energy. Hence we can state that the variance is an indicator of the potential energy of the system.

In Fig.(4.4) it is straightforward to notice that there is an increase of the variance proportional to the intensity of the distortion, represented by γ. Also, the particles in the middle of the chain seem more affected by the increase of the distortion with respect to the ones at the borders. Also in Fig.(4.5), there is a difference between the equilibrium and non equilibrium conditions: here, as we have said in Chapter 2, the Hamiltonian is expressed in normal modes, but as in the Cartesian coordinates, the variance is connected also to the energy. Therefore, what we can deduce from Fig. (4.4) is that non equilibrium conditions cause an increase of the energy, as in [21].

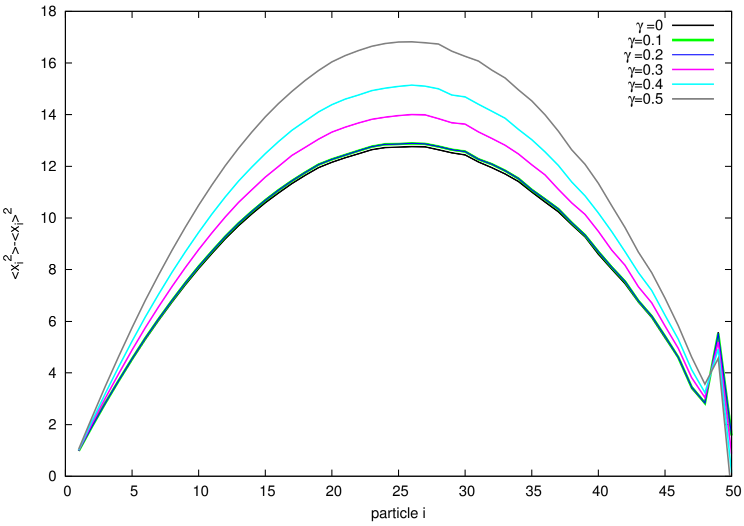


Figure 4.4: Variance of the Space Coordinates for different values of γ

The last observables we have analyzed are the ensemble average positions of the particles in the chain and the ensemble average distance between each other. We do not have comparison with other previous work we have studied since these kind of observables are not usually the most interesting for people who study oscillator chains. In fact one usually focuses their attention on the flux or on the energy in the chain but, since we are interested in the density distortion, we also consider these linear observables. In Fig.(4.6) the ensemble average position of particles is shown: it says that the density profile is practically constant for the harmonic case (Fig. 4.7), even if there is a temperature difference at the ends of the chain. This agrees with the formula in [22] and the theory of [13].

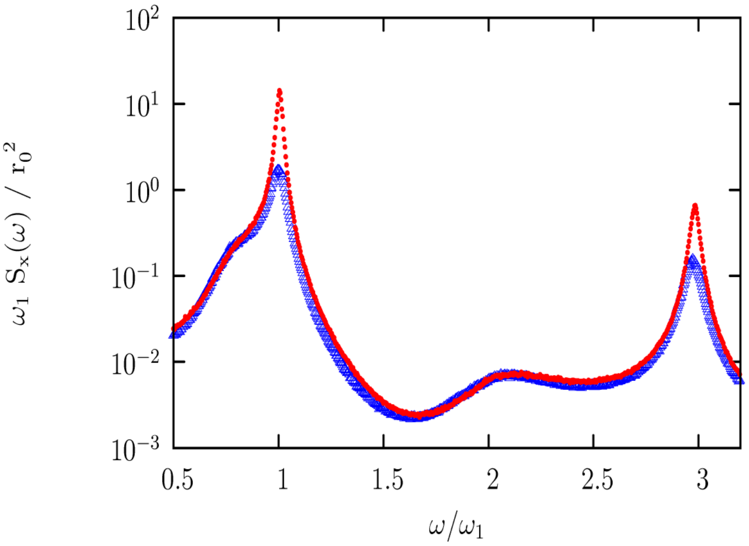


Figure 4.5: Variance of the Normal Modes in [21], where the blue and red lines represent respectively the equilibrium and non equilibrium situation (reproduced with the permission of *J. Stat. Mech.*)

Moreover, the temperature profile has also been studied numerically. In [22] the relation $\langle p_i^2 \rangle = \beta_1 \langle x_{i+1} - x_i \rangle + \beta_2$ has been found: in our case we can see from (4.7) that the observable $\langle x_{i+1} - x_i \rangle$ is the same for all values of γ, while in Fig.(4.1) the quantity $< v_i^2 >$ differs for the different values of γ only by a constant. This means that for us the relation above is reduced to $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle + \beta_2$, because β_1 is equal to 1.

In this case the parameter β_2 describes how the system is deviating from an ideal gas behavior: in fact we know that for ideal gas the following formula holds

$$PV = nRT \tag{4.11}$$

with P the pressure of the gas, V The volume, n the number of moles, T the temperature and the constant $R = 8.314$ J/mol K. For the chain

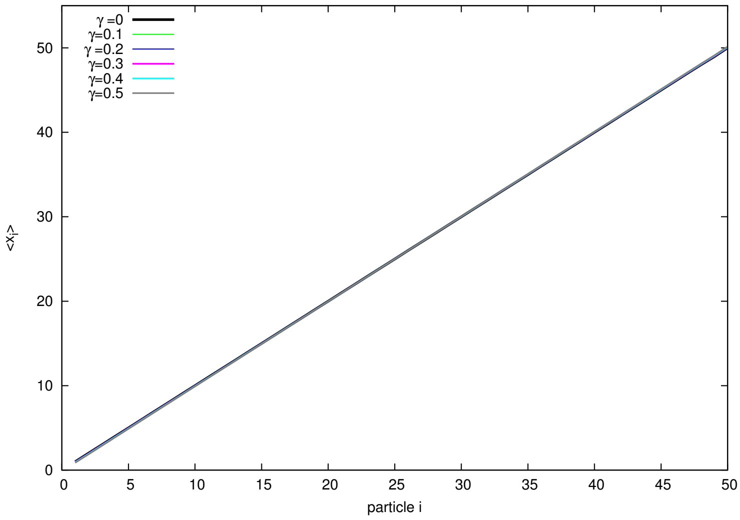


Figure 4.6: Ensemble Average Position of Particle i

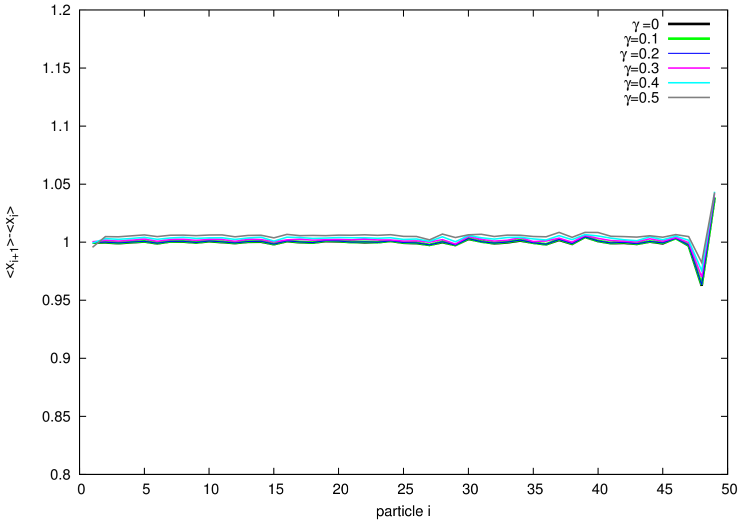


Figure 4.7: Ensemble Average of the distance Between two Particles

$V = 1/\langle x_{i+1} - x_i \rangle$ and $P \propto T \sim \langle p_i^2 \rangle$ and putting $n = 1$, the formula in (4.11) can be translated as

$$\langle p_i^2 \rangle \propto \langle x_{i+1} - x_i \rangle \tag{4.12}$$

the differs from the one we use for the term β_2.

As we can observe in Fig.(4.8), for $\gamma = 0$, β_2 is equal to zero and the two quantities coincide, except for the particles on the right edge.

For all the other cases represented in Fig.(4.9) $\langle v_i^2 \rangle$ and $\langle x_{i+1} - x_i \rangle$ differ by a constant which depends on the values of γ. In particular in Fig.(4.10) we can see the dependence of β_2 on γ and it is straightforward to realize that it is actually a quadratic dependence.

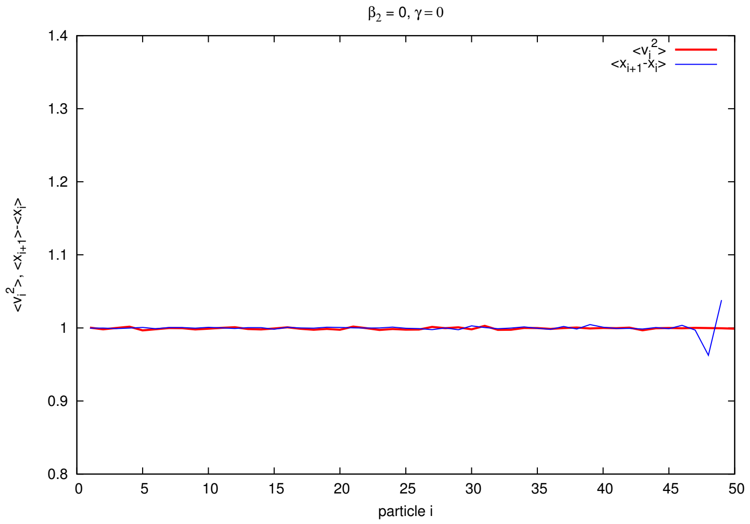
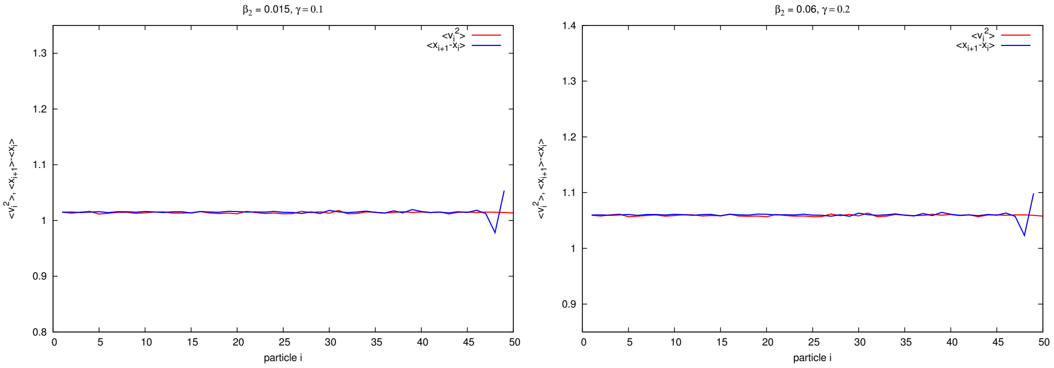


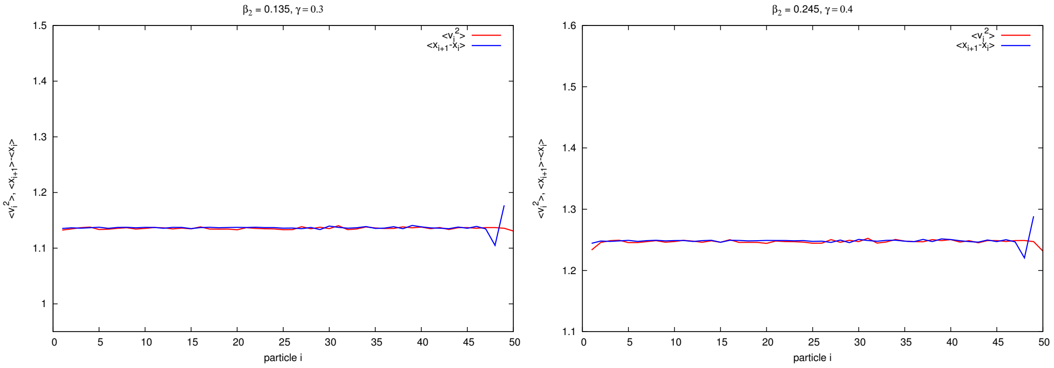
Figure 4.8: Relation $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle$ for $\gamma = 0$

4.5 Conclusions

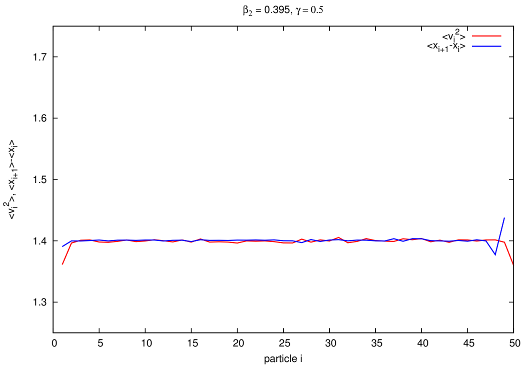
In this chapter we have tried to extrapolate some basic properties of the oscillator chain by running some numerical computations. We have first



(a) $\gamma = 0.1, \beta_2 = 0.015$ (b) $\gamma = 0.2, \beta_2 = 0.06$



(c) $\gamma = 0.3, \beta_2 = 0.135$ (d) $\gamma = 0.4, \beta_2 = 0.245$



(e) $\gamma = 0.5, \beta_2 = 0.395$

Figure 4.9: Relation $\langle v_i^2 \rangle = \beta_1 \langle x_{i+1} - x_i \rangle$ for different values of γ

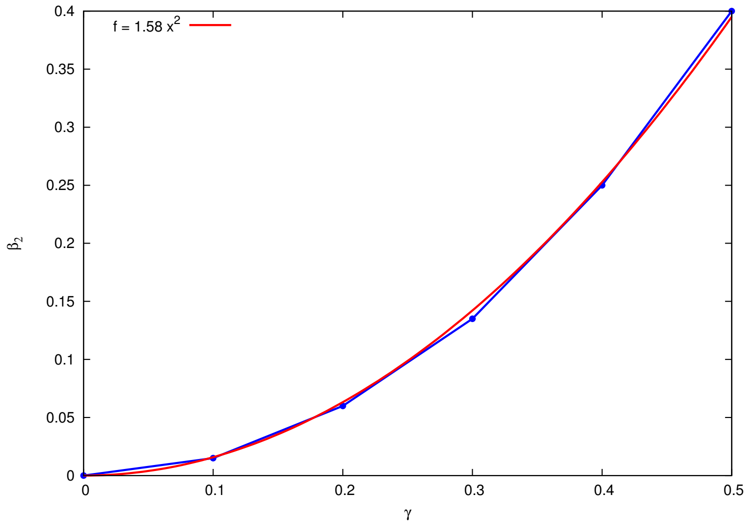


Figure 4.10: Dependence of β_2 on γ with fit with the function $f(x) = ax^2$ with $a = 1.58$

considered a 2-particle chain to be able to do a comparison with the analytical results of the previous chapter.

Once the agreement of the results was confirmed, we have run a simulation for a 50-particle system to understand the behavior of the observables that characterize the chain in relation to the intensity of the distortion, which means for different values of γ.

As we have explained in the introduction, chains of oscillators with harmonic potential (harmonic oscillator chains) have been deeply and widely studied in literature and exact analitycal solutions already exist.

The reason of this part of the work was in fact to check the agreement of our results, both analytical and numerical, with the ones already known to check the consistency of our model. If this was proved to be true than we could focus on other kind of potential, like the FPU potential, that does not have exact analytical results.

The observables we have considered in this chapter are the variance of the position, the kinetic temperature, the density of the chain and finally also the temperature profile. We have seen than the system, described with our model, shares indeed the same properties of the ones studied in [21,22,13] and that the dependence on the non equilibrium conditions is qualitatively the same.

Thanks to these promising results, in the second part of our work we can focus our attention on an oscillator chain characterized by a FPU potential to investigate if this model can be successful also in this case.

PART 2: FPU POTENTIAL

Chapter 5

Analytical Results

5.1 Introduction

In this second part of the work we are studing the chain of oscillators with a new potential: now in the Hamiltonian, instead of the harmonic one, we consider the so-called α-Fermi-Pasta-Ulam potential written in the following form

$$V(x) = \sum_{i=0}^{N} \left[\frac{k}{2}(x_{i+1} - x_i)^2 + \frac{k_3}{3}(x_{i+1} - x_i)^3 \right] \tag{5.1}$$

with N the number of particles, k and k_3 respectively the coupling constant of the quadratic and cubic terms. As before, the first step is to understand if exact analytical solutions are possible for some basic observables of the system with this new potential. In this case it is actually more important to investigate the existence of analytical solutions with respect to the previous case since as we have explained in the introduction, they haven't been found up to now for this kind of potential.

We begin again by considering a 2-particle system whose Hamiltonian is now

$$H = \sum_{i=0}^{2} \left[\frac{k}{2}(x_{i+1} - x_i)^2 + \frac{1}{3}k_3(x_{i+1} - x_i)^3 + \frac{m}{2}v_i^2 \right] \tag{5.2}$$

while the heat flux is the same as in (3.4), since the different potential does not affect the definition of the current that was built under very general conditions and is given by

$$J = -\frac{ka}{2}\left(v_1 x_2 - x_1 v_2 + L v_2\right) \tag{5.3}$$

5.2 Calculation of $\langle x_2 - x_1 \rangle$

5.2.1 Infinite Space Domain

We start our computation again with the quantity $\langle x_2 - x_1 \rangle$. That means we have to solve the following integral

$$\langle x_2 - x_1 \rangle = \frac{\int (x_2 - x_1) e^{-\beta H(x,v) - \gamma J(x,v)} dx dv}{\mathcal{K}} \tag{5.4}$$

with H is now given by (5.2), J by (5.3), $\Gamma = (x, v)$ is the phase space coordinates and $\mathcal{K}$ the new partition function. Explicitly the integral is

$$\begin{aligned}
\langle x_2 - x_1 \rangle &= \int (x_2 - x_1) \\
&\times \exp\left[-\beta k \left(x_1^2 + x_2^2 - x_1 x_2 - L x_2 + \frac{L^2}{2}\right)\right. \\
&+ \beta k_3 \left(x_1 x_2^2 - x_1^2 x_2 - L x_2^2 + L^2 x_2 - \frac{L^3}{3}\right) \\
&- \left.\frac{\beta m}{2}\left(v_1^2 + v_2^2\right) + \frac{\gamma k a}{2}\left(v_1 x_2 - x_1 v_2 + L v_2\right)\right] dx dv / \\
&\int \exp\left[-\beta k \left(x_1^2 + x_2^2 - x_1 x_2 - L x_2 + \frac{L^2}{2}\right)\right. \\
&+ \beta k_3 \left(x_1 x_2^2 - x_1^2 x_2 - L x_2^2 + L^2 x_2 - \frac{L^3}{3}\right) \\
&- \left.\frac{\beta m}{2}\left(v_1^2 + v_2^2\right) + \frac{\gamma k a}{2}\left(v_1 x_2 - x_1 v_2 + L v_2\right)\right] dx dv
\end{aligned} \tag{5.5}$$

We first try to compute the partition function $\mathcal{K}$, which means the integral in the denominator of (5.5).

We start by integrating in the variable v_1

$$\int e^{-\frac{\beta m}{2}v_1^2+\frac{\gamma ka}{2}x_2v_1}dv_1 = \sqrt{\frac{2\pi}{\beta m}}e^{\frac{a^2\gamma^2k^2}{8\beta m}x_2^2} \tag{5.6}$$

and then the variable v_2

$$\begin{aligned}\int e^{-\frac{\beta m}{2}x_2^2-\frac{\gamma ka}{2}x_1v_2+\frac{\gamma ka}{2}Lv_2}dv_2 &= \sqrt{\frac{2\pi}{\beta m}}e^{\frac{a^2\gamma^2k^2}{8\beta m}(L-x_1)^2} \\ &= \sqrt{\frac{2\pi}{\beta m}}e^{\frac{a^2\gamma^2k^2}{8\beta m}L^2+\frac{a^2\gamma^2k^2}{8\beta m}x_1^2-\frac{a^2\gamma^2k^2}{4\beta m}Lx_1}\end{aligned} \tag{5.7}$$

The result in (5.6) and (5.7) are possible under the costraint

$$-\frac{\beta m}{2} < 0 \tag{5.8}$$

which is always true, since β and m are positive.

We can now move to the space coordinates, starting with x_1

$$\begin{gathered}\int e^{-\beta kx_1^2+\beta kx_1x_2+\beta k_3x_1x_2^2-\beta k_3x_2x_1^2+\frac{a^2\gamma^2k^2}{8\beta m}x_1^2-\frac{a^2\gamma^2k^2}{4\beta m}Lx_1}dx_1 = \\ \frac{2\sqrt{2\pi}}{\sqrt{-\frac{a^2\gamma^2k^2}{\beta m}+8\beta(k+k_3x_2)}}e^{-\frac{(a^2\gamma^2k^2L-4\beta^2mx_2(k+k_3x_2))^2}{8\beta m(a^2\gamma^2k^2-8\beta^2m(k+k_3x_2))}} = \\ \frac{2\sqrt{2\pi}}{\sqrt{-\frac{a^2\gamma^2k^2}{\beta m}+8\beta(k+k_3x_2)}}\times \\ e^{\frac{-a^4\gamma^4k^4L^2-16\beta^4m^2k^2x_2^2-16\beta^4m^2k_3^2x_2^4+8\beta^2a^2\gamma^2k^3Lmx_2+8\beta^2a^2\gamma^2k^2k_3mLx_2^2-32\beta^4m^2kk_3x_2^3}{8\beta m(a^2\gamma^2k^2-8\beta^2m(k+k_3x_2))}}\end{gathered} \tag{5.9}$$

It is crucial now to underline that this result is possible with a restriction not only on the parameter space but also on the variable x_2. In fact the following inequality is needed

$$-\beta k - \beta k_3x_2 + \frac{a^2\gamma^2k^2}{8\beta m} < 0 \tag{5.10}$$

which is translated in a constraint in the x_2 variable

$$x_2 > \frac{a^2\gamma^2k^2}{8\beta^2k_3m} - \frac{k}{k_3} \tag{5.11}$$

This is a different consequence from the constraints we encountered in Chapter 3: in fact in that case the constraints were only on the parameter space, while now it is on the *domain* on a variable.

This means that the partition function, and consequently the integral, diverges because in the model considered the range of the variable x_2 includes the whole phase space and no restrictions are present.

5.2.2 Restricted Space Domain

Since the system with a α-FPU potential is not normalizable, it is not suitable to describe chains of particles which are free to space on the whole real line.

On the other hand, from a physical point of view, confined systems between two walls are usually more interesting and more realistic. Therefore we can consider a restricted domain for the space variables, while there is no constraint on the value of the velocities.

It is straightforward to decide the boundaries of our new domain: since we are considering a chain of length L and the Hamiltonian is written with the Cartesian axis starting from 0, then the domain for the x_1 and x_2 variables will be $[0, L]$.

The computation of $\langle x_2 - x_1 \rangle$ is the same for v_1 and v_2 so we obtain the same results as in (5.6) and (5.7). We can consider the integral of the two space variables together which means

$$\begin{aligned}\int_0^L \int_0^L \exp \quad & \Big[-\beta k x_1^2 - \beta k x_2^2 + \beta k_3 x_1 x_2^2 - \beta k_3 x_1^2 x_2 \\ & + \beta k x_1 x_2 + \beta k L x_2 + \beta k_3 L^2 x_2 - \beta k_3 L x_2^2 \\ & + \frac{a^2\gamma^2 k^2}{8\beta m} x_1^2 - \frac{a^2\gamma^2 k^2}{4\beta m} L x_1 + \frac{a^2\gamma^2 k^2}{8\beta m} x_2^2 \Big] dx_1 dx_2 \qquad (5.12)\end{aligned}$$

We did not succeed in finding the primitive of the integrand. However, as we have done in the previous section, we can do some consideration on the convergence of the integral in (5.12).

We are now dealing with an integrand that is a continuous function in two variables in a compact domain: hence, the convergence of the integral is guaranteed.

5.3 Conclusions

In this Chapter we have considered the Fermi-Pasta-Ulam potential instead of the harmonic one and we have tried to understand if exact analytical solutions exist for the observables of this system.

Because of the new cubic terms in the potential we encountered some obstacles because the partition function does not converge in the whole phase space.

For this reason we have decided to restrict the space domain to the interval $[0, L]$, with L the length of the chain, which is a reasonable choice since the edges of the chain are fixed. In this case the convergence is assured, still we were unable to find the primitive of the integrand and consequently we were not able to find exact analytical solutions for the observables the characterize this system, even in a confined space domain.

This means we are going to study the system only through numerical calculation in the following chapter.

Chapter 6

Numerical Results

6.1 Introduction

We have proved in the previous chapter that exact analytical solutions are not possible for a chain of oscillators with a FPU potential. Nevertheless we know that the integral used to compute the observables converges if we consider a restricted space domain, still we do not know their exact values. Hence the next step is to try to compute numerically these quantities since, as explained in Chapter 4, Monte Carlo simulation is used to obtain the value of an integral without explicitly knowing the primitive of the integrand. In this case we are dealing with problems not previously considered. In fact, in Chapter 4, to compute the ensemble average of an observable A, we used the formula (4.5)

$$\langle A \rangle = \frac{\int A(\xi) e^{-\beta H(\xi) - \gamma J(\xi)} d\xi}{\mathcal{K}} \tag{6.1}$$

with $\xi = (x, v)$ the spatial and momentum coordinates in the phase space and $\mathcal{K}$ the partition function and where the probability density was given by (4.6)

$$\rho(\xi) = \frac{e^{-\beta H(\xi) - \gamma J(\xi)}}{\mathcal{K}} \tag{6.2}$$

and it was considered as the Gaussian distribution of the initial random vectors ξ. Afterwards, we built the covariance matrix Σ and the average μ of the distribution by using the equality (4.9)

$$-\frac{1}{2}(\xi-\mu)^T\Sigma^{-1}(\xi-\mu) = -\beta H(\xi) - \gamma J(\xi) \tag{6.3}$$

where the quadratic terms were considered in the covariance matrix and the linear ones in the average.

The change in potential causes not only some difference in the analytical computation but also in the Monte Carlo simulations. In fact, if we consider for example a 2-particle system with the FPU potential we know that some cubic terms arise (5.1)

$$V(x) = \sum_{i=0}^{2}\left[\frac{1}{2}k(x_{i+1}-x_i)^2 + \frac{1}{3}k_3(x_{i+1}-x_i)^3\right] =$$

$$k(x_1^2+x_2^2-x_1x_2-Lx_2+\frac{L^2}{2}) + k_3(x_1x_2^2-x_1^2x_2-Lx_2^2+L^2x_2-\frac{L^3}{3}) \tag{6.4}$$

that cannot be considered in Σ nor in μ. A solution of this problem is to consider in (6.3) only the quadratic and linear terms that arise from $-\beta H(\xi) - \gamma J(\xi)$ and to study the cubic terms $k_3(x_1x_2^2 - x_1^2x_2)$ together with the observable A so that the integral becomes

$$\langle A\rangle = \frac{\int A(\xi)e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi}{\int e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi} \tag{6.5}$$

where Δ contains all the linear and quadratic terms that arise from the right hand side of (6.3). We can now manipulate (6.5) in the following way

$$\begin{aligned}
\langle A\rangle &= \frac{\int A(\xi)e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi}{\int e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi} \\
&= \frac{\int A(\xi)e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi}{\int e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi}\frac{\int e^{\Delta}d\xi}{\int e^{\Delta}d\xi} \\
&= \frac{\int A(\xi)e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi}{\int e^{\Delta}d\xi}\frac{\int e^{\Delta}d\xi}{\int e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}e^{\Delta}d\xi} \\
&= \frac{\int A(\xi)e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}\rho'(\xi)d\xi}{\int e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}\rho'(\xi)d\xi} = \frac{\langle Ae^{-\beta k_3(x_1x_2^2-x_1^2x_2)}\rangle_{\rho'}}{\langle e^{-\beta k_3(x_1x_2^2-x_1^2x_2)}\rangle_{\rho'}}
\end{aligned} \tag{6.6}$$

with $\rho'(\xi) = \frac{e^{\Delta}}{\int e^{\Delta} d\xi} = \frac{e^{\Delta}}{\mathcal{K}'}$ the new distribution function and $\mathcal{K}'$ the new partition function. This means that the final result is

$$\langle A \rangle_{\rho} = \frac{\left\langle A e^{-\beta k_3 (x_1 x_2^2 - x_1^2 x_2)} \right\rangle_{\rho'}}{\left\langle e^{-\beta k_3 (x_1 x_2^2 - x_1^2 x_2)} \right\rangle_{\rho'}} \tag{6.7}$$

6.2 50-Particle System

We have seen in Chapter 5 that exact analytical solutions for the observables that characterize the system are not possible with a α-FPU potential.

The consequence is that we cannot do a comparison, as we did in Chapter 4, between the analytical and numerical results: in this case we are just going to evaluate the observables numerically for a 50-particle system.

The observables considered are the same as in the harmonic potential case, here we have studied the system for three different values of the coupling constant k_3 of the FPU potential: $0.001, 0.002$ and 0.003, while k, the coupling constant of the quadratic term, is still set to 1.

We have chosen small values of k_3 because our interest is to understand how the properties of system change as we slowly move from the harmonic case, which is the one known.

For all the observables it is straightforward to notice that if we set $k_3 = 0.001$ the behavior is similar to the harmonic case, while, as the value of k_3 increases it becomes more and more irregular, while we know that from the physical point of view a smooth trend is expected. The reason is that, as we move from the harmonic case better statistics, which means a higher number of samples, are needed to run to sufficient accuracy the Monte Carlo simulations.

In fact we have noticed that by increasing the number of samples the observables becomes smoother: in this work, we do not have the efficiency required to increase the number of samples for all the observables to a value that would be suitable for the case with $k_3 = 0.002$ and $k_3 = 0.003$.

Nevertheless, even in this case, one can notice that the dependence on the non equilibrium conditions is similar to the harmonic case: in fact the momentum and the variance of the space variables are increasing as γ takes higher values, while the ensemble average of the position and of the distance between two particles do not seem affected by γ.

For this reason we can say that the model, at least qualitatively, seems to share the same properties as in [21,22], concerning the dependence on non equilibrium conditions for systems with FPU potential.

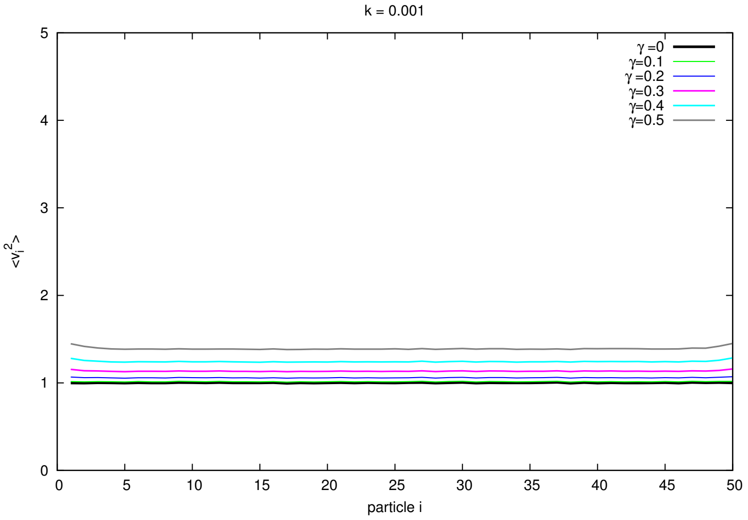


Figure 6.1: Ensemble Average of the Momentum of the i particle for different values of γ and with $k_3 = 0.001$

Finally, we have taken into account the temperature profile: the steps are the same as in Chapter 4, beginning with the case with $\gamma = 0$. Also here we consider the relation $\langle v_i^2 \rangle = \beta_1 \langle x_{i+1} - x_i \rangle + \beta_2$, with $\beta_1 = 1$. Also here β_2

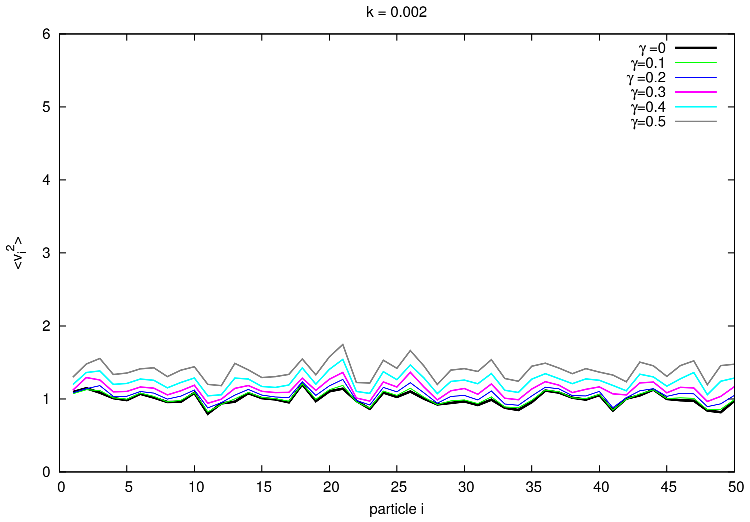


Figure 6.2: Ensemble Average of the Momentum of the i particle for different values of γ and with $k_3 = 0.002$

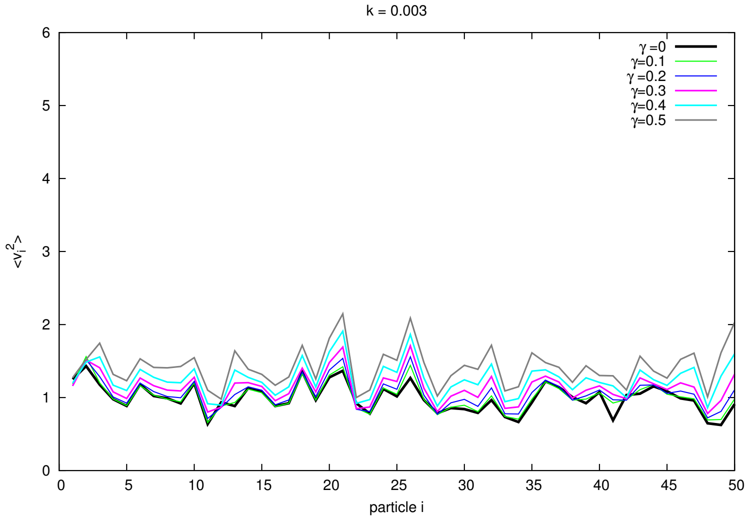


Figure 6.3: Ensemble Average of the Momentum of the i particle for different values of γ and with $k_3 = 0.003$

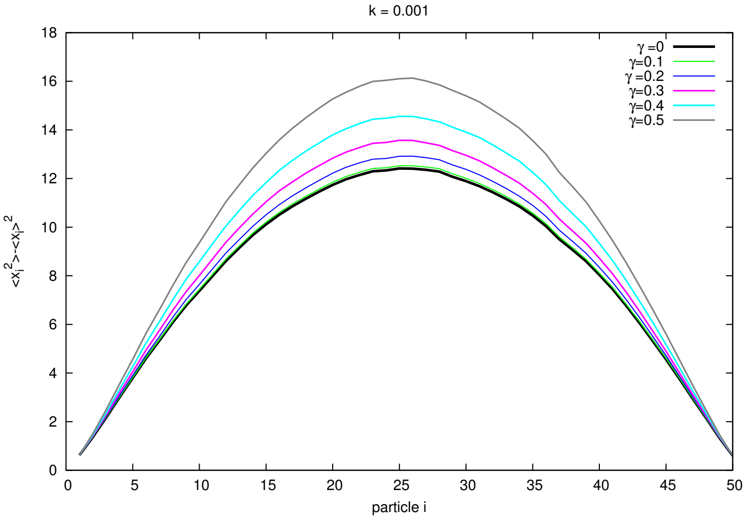


Figure 6.4: Variance of the Space Coordinates for different values of γ and with $k_3 = 0.001$

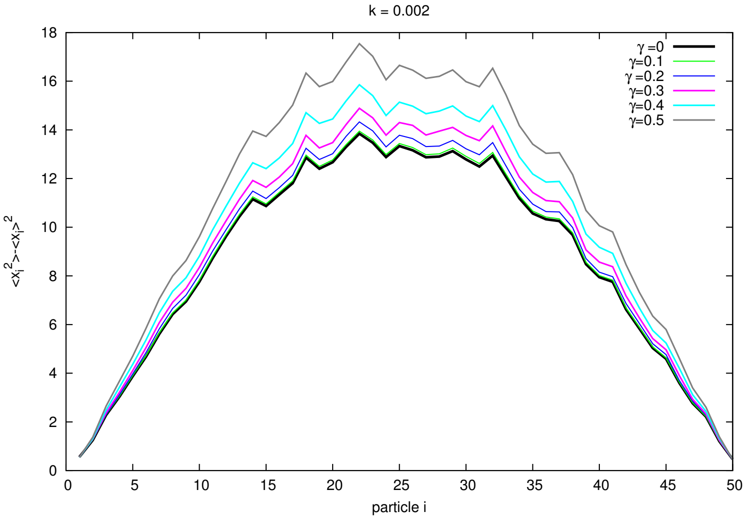


Figure 6.5: Variance of the Space Coordinates for different values of γ and with $k_3 = 0.002$

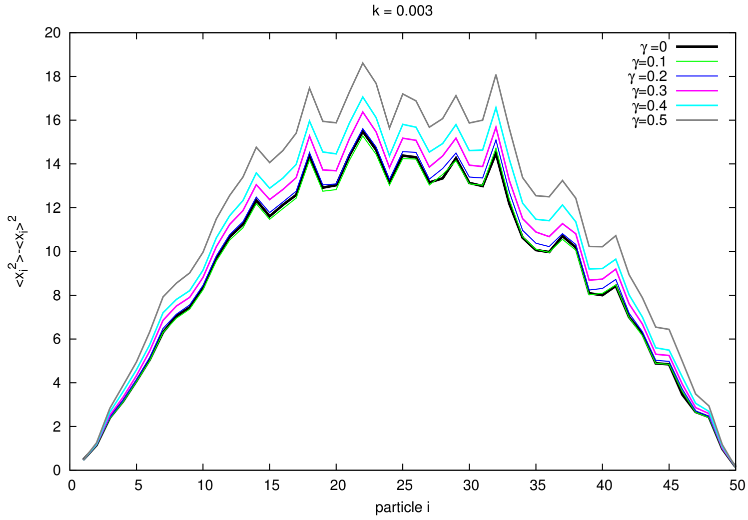


Figure 6.6: Variance of the Space Coordinates for different values of γ and with $k_3 = 0.003$

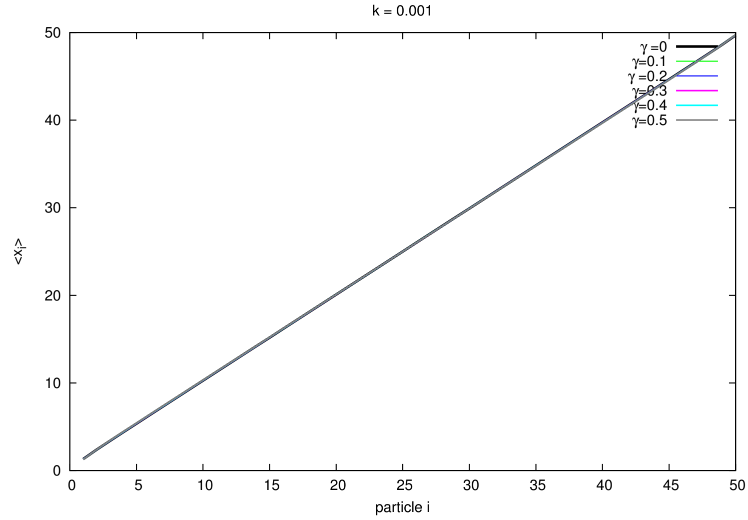


Figure 6.7: Ensemble Average Position of Particle i for different values of γ and with $k_3 = 0.001$

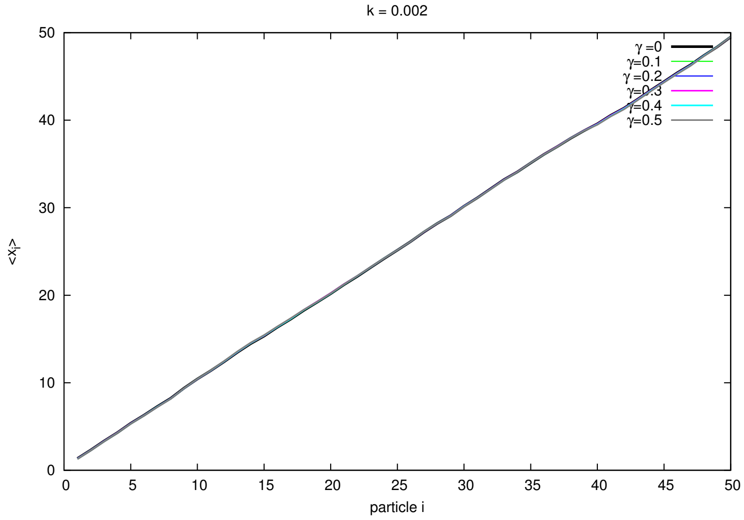


Figure 6.8: Ensemble Average Position of Particle i for different values of γ and with $k_3 = 0.002$

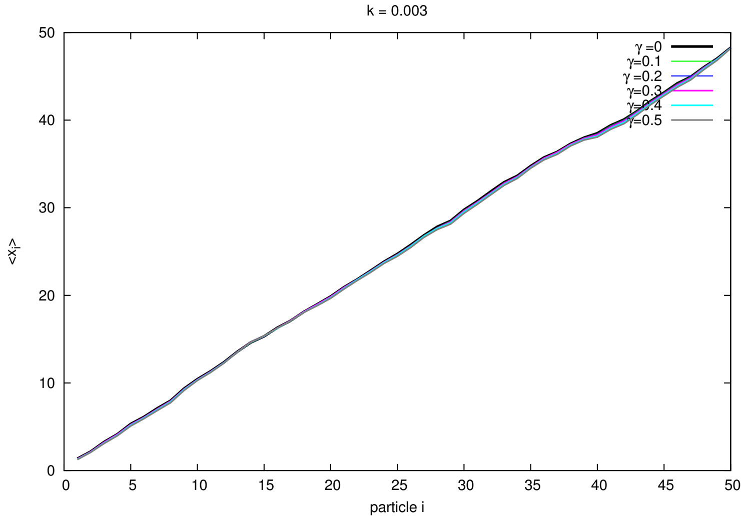


Figure 6.9: Ensemble Average Position of Particle i for different values of γ and with $k_3 = 0.003$

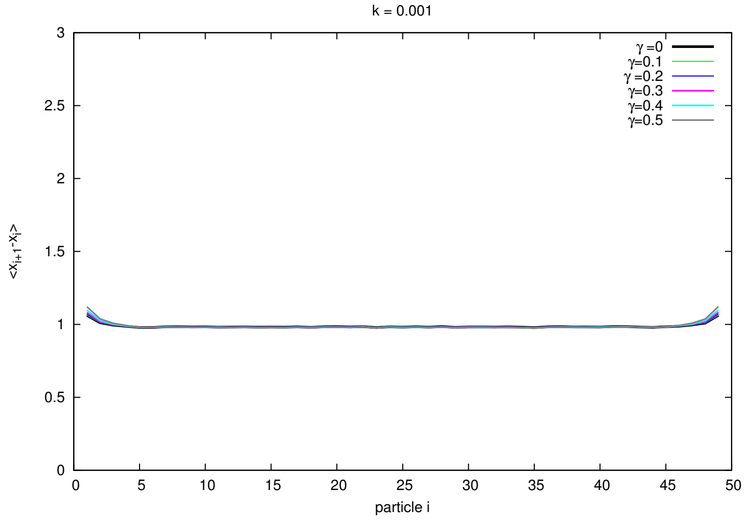


Figure 6.10: Ensemble Average of the distance Between two Particles for different values of γ and with $k_3 = 0.001$

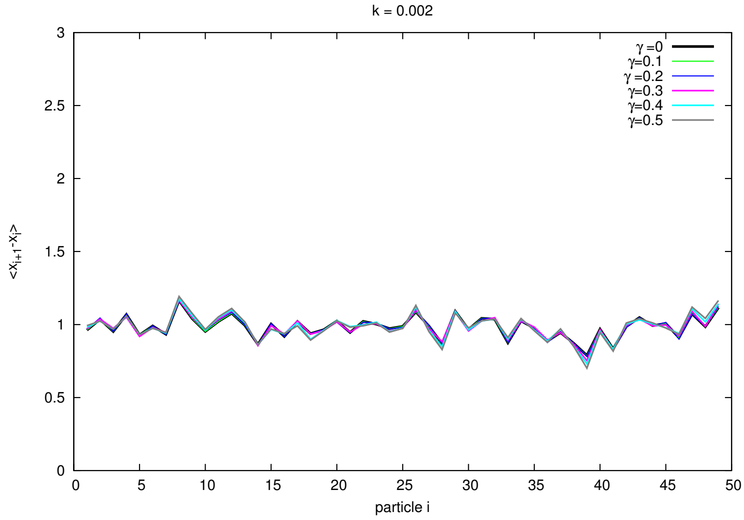


Figure 6.11: Ensemble Average of the distance Between two Particles for different values of γ and with $k_3 = 0.002$

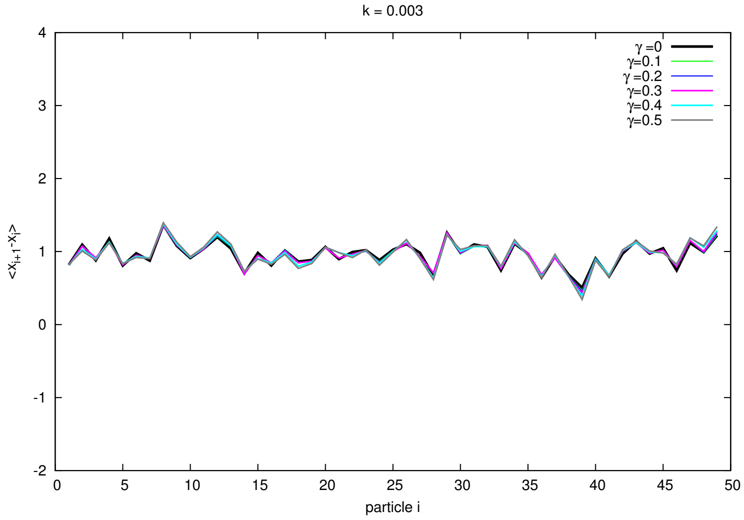


Figure 6.12: Ensemble Average of the distance Between two Particles for different values of γ and with $k_3 = 0.003$

represents the deviation from an ideal gas behavior.

We have started with $k_3 = 0.001$ where it is possible to notice that, unlike the harmonic case, for $\gamma = 0$, β_2 is not zero. Also here we have shown the dependence of β_2 on γ that can be approximated to a parabola. For the cases with $k_3 = 0.002$ and $k_3 = 0.003$ it is not possible to do a comparison between the data of the observables $\langle v_i^2 \rangle$ and $\langle x_{i+1} - x_i \rangle$ due to their irregular behavior. Hence it is necessary to first approximate the trend of this observables to a constant, which is the expected approximated behavior. Afterwards we compare the approximations for the different values of γ to get β_2. The results are shown in figures (6.16) and (6.18).

Also, in figures (6.17) and (6.19) it is straightforward to see that the dependence of β_2 on γ can be approximated to a parabola.

Finally we compared the dependence of β_2 on γ for all the cases we studied. In figure (6.20) the case with the harmonic potential and with the

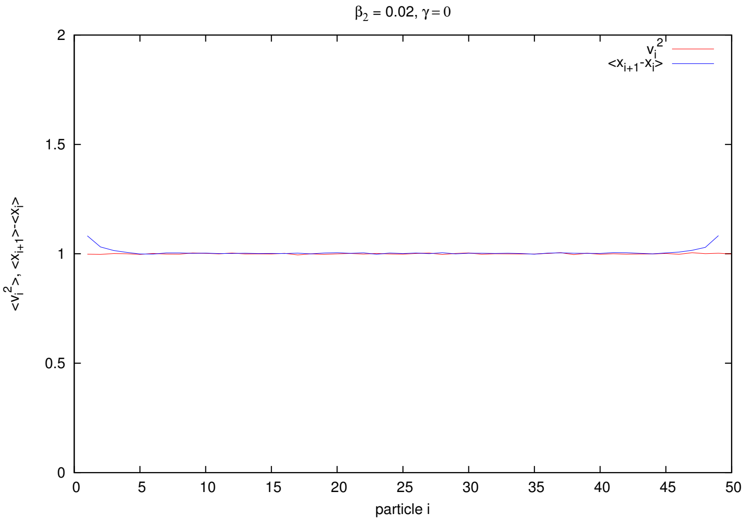


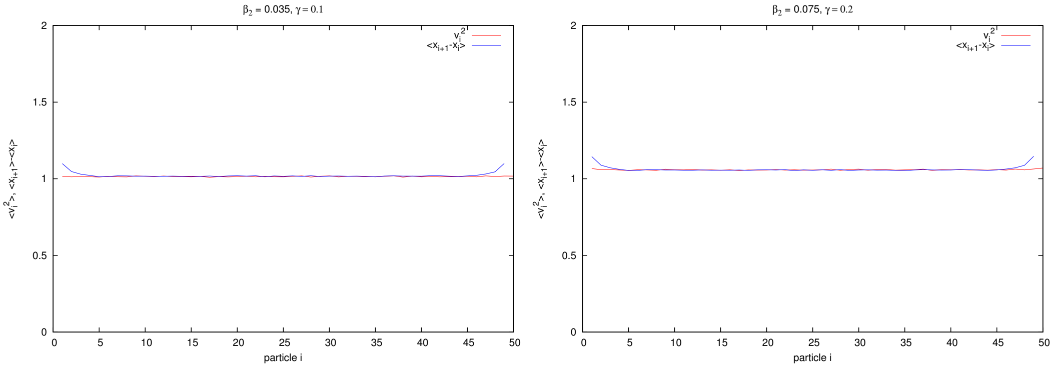
Figure 6.13: Relation $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle$ for $\gamma = 0$ and with $k_3 = 0.001$

three values for the FPU potential is shown: as we said before β_2 has a quadratic dependence on γ and its values are increasing as we move away from the harmonic case.

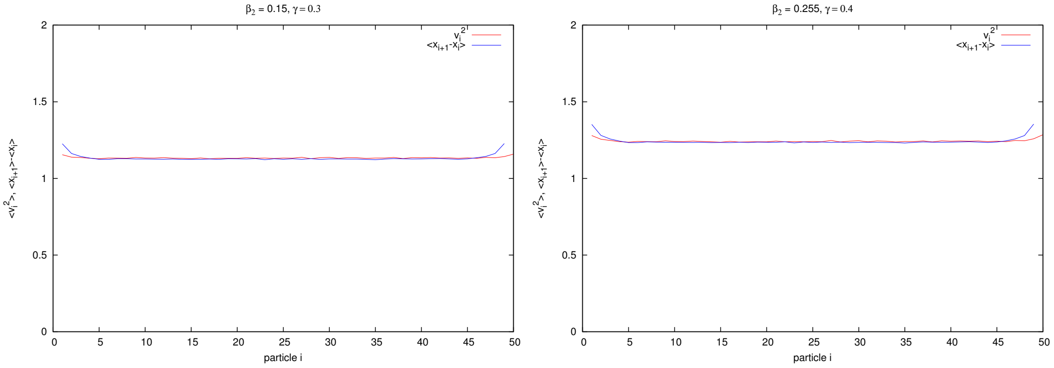
6.3 Conclusions

In this Chapter we have computed numerically the same observables as in Chapter 4 with a different potential. Here we have chosen three values for the coupling constant of the cubic term: we have noticed that, in the $k_3 = 0.001$ case, the behaviour of the observables is similar to the harmonic case, while for the other two values the trend proved to be quite irregular, due to a lack of statistics.

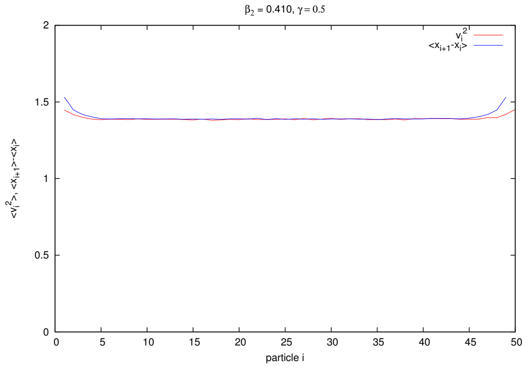
Nevertheless in all three cases it was possible to see that the dependence of the observables on the non equilibrium condition is the qualitatively the same as in the harmonic case and in [21,22].



(a) $\gamma = 0.1, \beta_2 = 0.015$ (b) $\gamma = 0.2, \beta_2 = 0.06$



(c) $\gamma = 0.3, \beta_2 = 0.135$ (d) $\gamma = 0.4, \beta_2 = 0.245$



(e) $\gamma = 0.5, \beta_2 = 0.395$

Figure 6.14: Relation $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle + \beta_2$ for different values of γ and with $k_3 = 0.001$

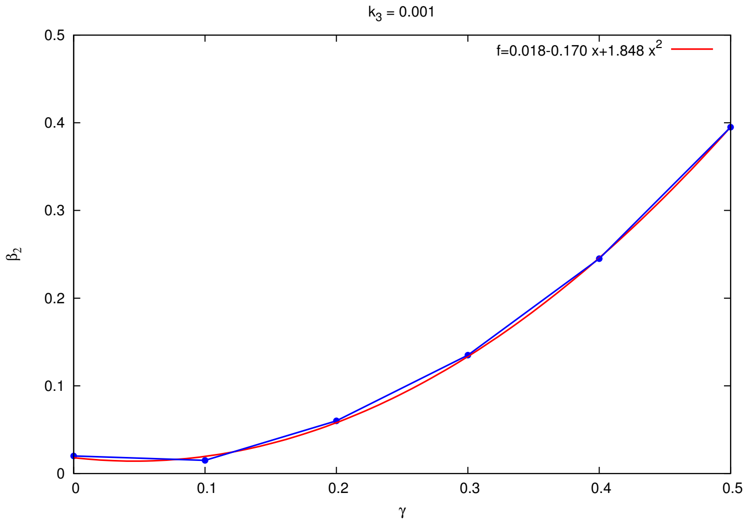
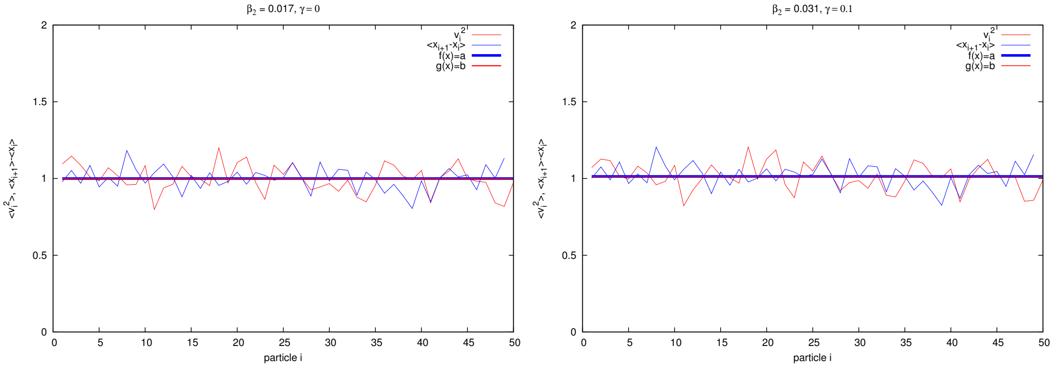
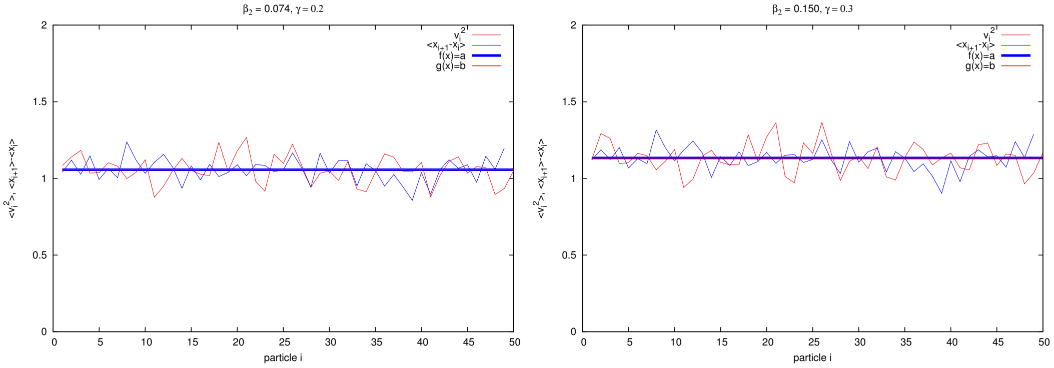


Figure 6.15: Dependence of β_2 on γ with fit with the function $f(x) = c + bx + ax^2$ with $a = 1.848$, $b = -0.170$ and $c = 0.018$

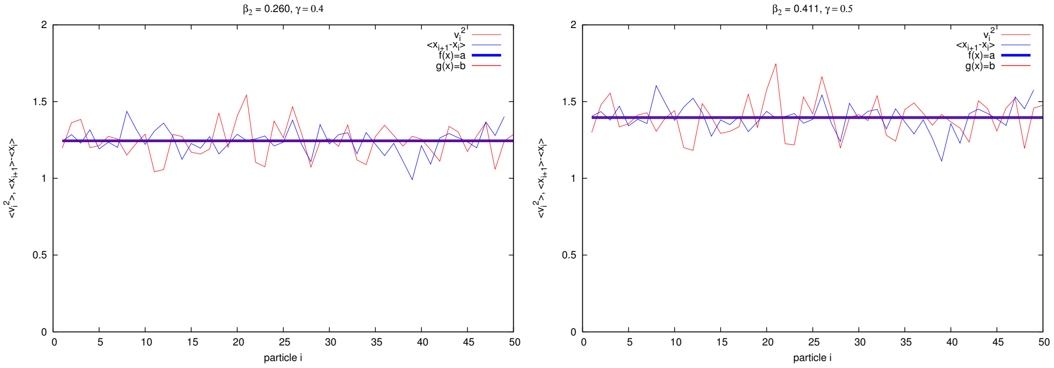
Finally we have also computed the temperature profile and checked the relation between β_2 and γ that for all the three values of the coupling constant can be approximated to a parabola, with the value of β_2 increasing with the coupling constant of the cubic term k_3.



(a) $\gamma = 0, \beta_2 = 0.017$ (b) $\gamma = 0.1, \beta_2 = 0.031$



(c) $\gamma = 0.2, \beta_2 = 0.074$ (d) $\gamma = 0.3, \beta_2 = 0.150$



(e) $\gamma = 0.4, \beta_2 = 0.260$ (f) $\gamma = 0.5, \beta_2 = 0.411$

Figure 6.16: Relation $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle + \beta_2$ for different values of γ and with $k_3 = 0.002$

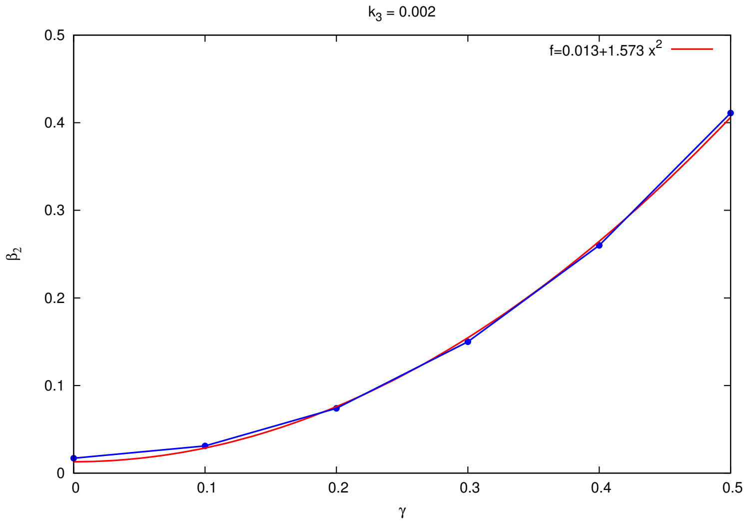
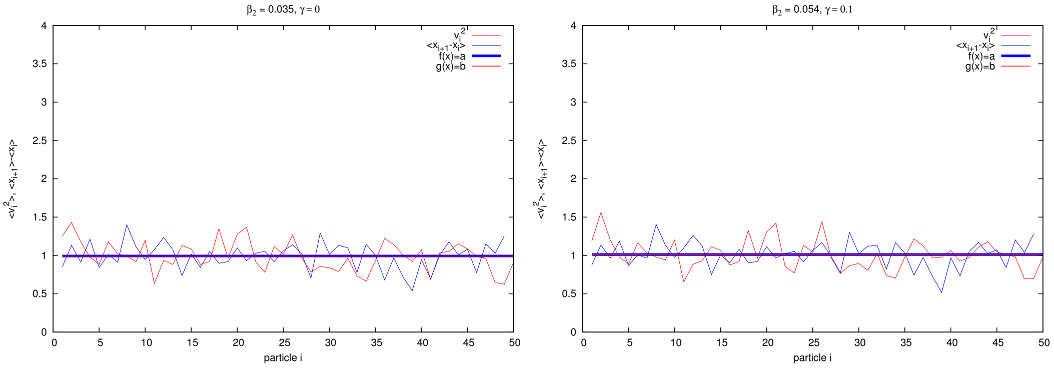
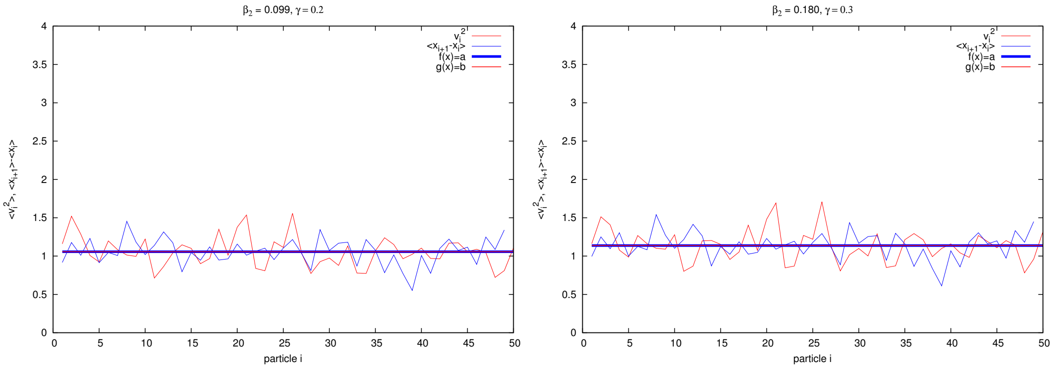


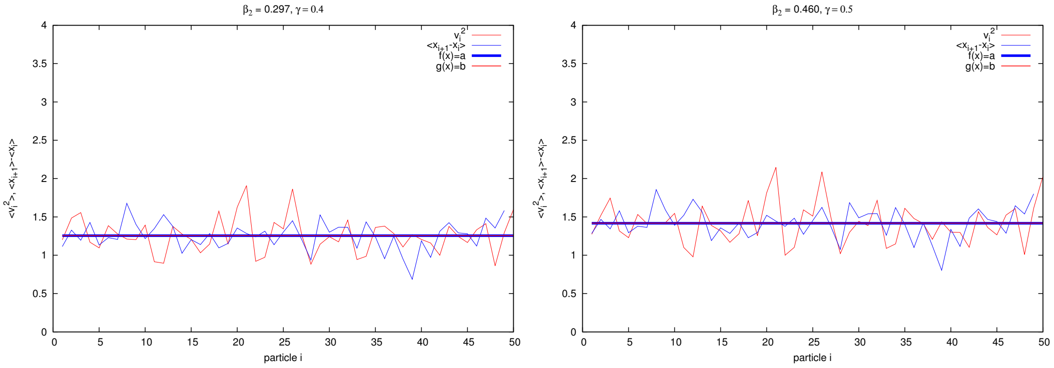
Figure 6.17: Dependence of β_2 on γ with fit with the function $f(x) = b + ax^2$ with $a = 1.573$ and $b = 0.013$



(a) $\gamma = 0, \beta_2 = 0.035$ (b) $\gamma = 0.1, \beta_2 = 0.054$



(c) $\gamma = 0.2, \beta_2 = 0.099$ (d) $\gamma = 0.3, \beta_2 = 0.180$



(e) $\gamma = 0.4, \beta_2 = 0.297$ (f) $\gamma = 0.5, \beta_2 = 0.460$

Figure 6.18: Relation $\langle v_i^2 \rangle = \langle x_{i+1} - x_i \rangle + \beta_2$ for different values of γ and with $k_3 = 0.003$

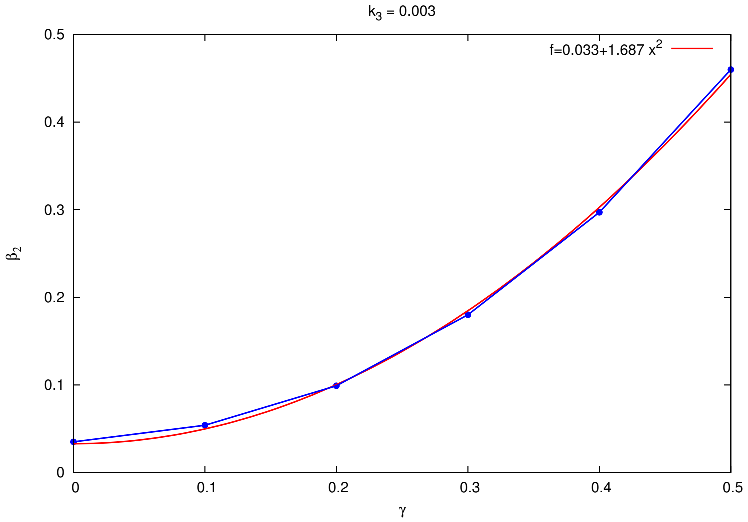


Figure 6.19: Dependence of β_2 on γ with fit with the function $f(x) = b + ax^2$ with $a = 1.687$ and $b = 0.033$

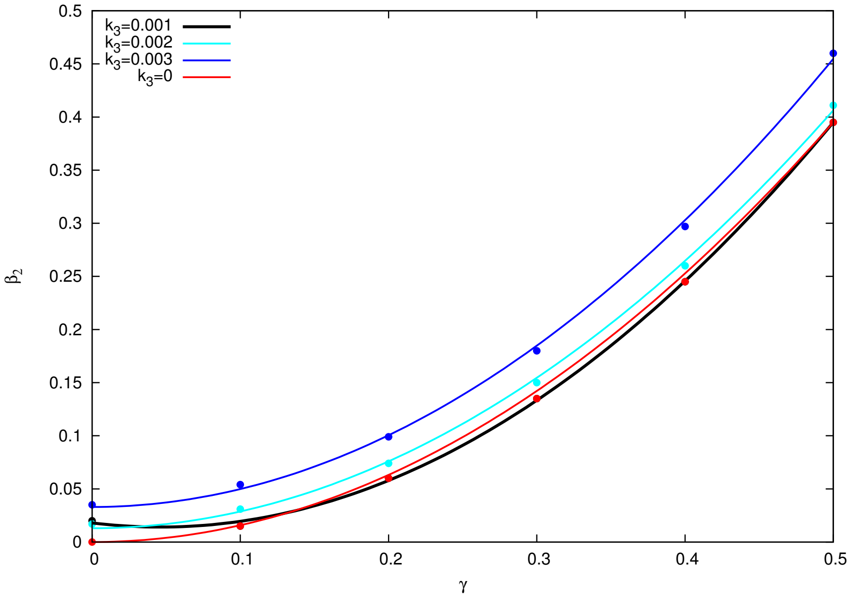


Figure 6.20: Dependence of β_2 on γ for the harmonic and FPU potential case

Chapter 7

Conclusions

7.1 Conclusions

In this thesis we have dealt with low dimensional systems in non equilibrium conditions, which possess some peculiar characteristics in comparison to systems with a higher number of degrees of freedom.

In particular, we have focused our attention on a 1-dimensional chain of oscillators, hence with a phase space of $2N$ degrees of freedom, with N the number of particles, and we have tried to extrapolate some properties of this physical system by computing some basic observables that characterize the chain.

Actually, this kind of system has been studied deeply in literature: our purpose was in fact to find an alternative model to describe it, instead of the usual ones as explained in the introduction.

One of the reason was to find an easier way to study oscillator chains both from the analytical and numerical point of view.

In the first part of the thesis the attention was focused on a harmonic oscillator chain, which means on a chain with a harmonic potential: in this case not only numerical but also exact analytical solutions already exist. Indeed we have used the harmonic chain as a check, to understand if our results were in agreement with the known ones and, as a consequence, if our model could be considered consistent.

We have started in Chapter 3 with the computation of the analytical solutions of some basic observables for a 2-particle system and we have proved that exact solutions exist for this model but only under some constraints on the parameter space.

The quantities considered were the kinetic temperature, the variance of the space variables, the average position of the particles and the average of the distance between two particles.

We have then studied the same observables in Chapter 4 for a 50-particle system by running some Monte Carlo simulations; the results were quite promising: the qualitative behavior of all the quantities considered proved to be similar to the ones obtained in [21,22,13].

From the numerical point of view we have also considered the temperature profile to check if the relation $\langle v_i^2 \rangle = \beta_1 < x_{i+1} - x_i > +\beta_2$ in [22] could also be applied in our case. Indeed the relation still stands for our model with $\beta_1 = 1$ and β_2 having a quadratic dependence on γ.

Given the promising results with the harmonic potential, in the second part of the thesis, we have considered a different potential for the chain: an α-FPU potential. In this case exact analytical solutions do not exist yet and in Chapter 5 we have tried to understand if with this model it was possible to overcome this problem, by computing the observables as in Chapter 3: we indeed did not succeed in this task, even if some approximated solutions can be obtained by considering a restricted phase space.

In Chapter 6 we have then run the numerical simulations for the 50-particle system: here we have used three values of the coupling constant k_3 of the cubic term in the FPU-potential because our interest was to understand how the system was changing as we slowly moved away from the harmonic case. For $k_3 = 0.001$ it was straightforward to notice that the behavior was similar to the harmonic case for all variables, while for $k_3 = 0.002$ and $k_3 = 0.003$ the trend proved to be more irregular.

This was due to a lack of numerical efficiency since a higher number of samples is needed in the Monte Carlo simulations for higher values of k_3. Anyway, the dependence of these quantities on the non equilibrium conditions, for all the three values was the same as in the harmonic case with the momentum and the variance increasing with the intensity of the distortion. Finally, by studing the temperature profile, we could see that also the dependence of β_2 on γ was the same, with $\beta_1 = 1$ and β_2 with a quadratic dependence on γ and increasing as we moved away from the harmonic case.

7.2 Further Studies

In this work we have dealt with an oscillator chain with different kind of potential by using an alternative model with respect to the most common ones. The results we have obtained so far are quite promising but some issues remain still open.

First of all we have seen in Chapter 6 that with the values $k_3 = 0.002$ and $k_3 = 0.003$ in the α-FPU potential the behavior of the observables proved to be quite irregular. As we have explained this is due to a lack of efficiency in the numerical computations: it would be interesting to investigate this problem further by increasing the number of samples.

Moreover, we have considered only the α-FPU potential, which means the FPU potential with only the quadratic and the cubic terms. One possible step further could be to study also the β-FPU model, in which the quartic term is considered, instead of the cubic ones. This model is actually more widespread and more used to study physical system: hence including this potential would be a natural consequence of the path we have traced so far. Finally, an engaging to task would be to extend this model, which concerns only classical mechanics, to a quantum one to investigate the potentials of this model also in the subatomic case.

Appendix A

Normal Modes

A.1 Theoretical Calculation

We are going to give an overview of the theoretical calculation of the normal modes, with reference to [30]. In this section we are treating the general case while in the next one we will describe the whole procedure for a 2-particle system, whose properties are illustrated in Chapter 2.

Before dealing with the computation, it is important to understand what a normal mode is. A *normal mode* of an oscillating system is a kind of motion where all the components of the system move with the same frequency and with a fixed phase relation. Every normal mode has its fixed frequency which is called natural frequency or *resonant frequency*. Usually the motion of a system is a *superposition* of normal modes: these modes are independent, meaning they are orthogonal to each other.

This is one of the reason why they are often used to describe physical systems: if normal coordinates are used then the Lagrangian or the Hamiltonian of the system will be in diagonal form, a fact that will simplify the calculation.

Consider now a general system of N particles: we are treating system close to equilibrium. The condition for equilibrium is that the sum of the generalized or Cartesian coordinates that act on the system is zero, which means

$$\left(\frac{\partial V}{\partial x_i}\right)_0 = 0 \tag{A.1}$$

with x_i, the generalized coordinate of the ith-particle and V the potential energy. The displacement from the equilibrium position is defined as

$$\eta_i = x_i - x_{0i} \tag{A.2}$$

with x_{0i} the equilibrium position of the i particle. We can now make a Taylor expansion of the potential energy V around the equilibrium position

$$\begin{aligned} V(x_1 ... x_N) &= V(x_{01} ... x_{0N}) + \left(\frac{\partial V}{\partial x_i}\right)_0 (x_i - x_{i0}) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x_j x_i}\right)(x_i - x_{i0})^2 + ... \\ &= V(x_{01} ... x_{0N}) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial x_j x_i}\right)\eta_i\eta_j + o(\eta^2) \end{aligned} \tag{A.3}$$

since $V(x_{01} ... x_{0N})$ is a constant we can put it equal to zero and we obtain the relation

$$V = \frac{1}{2}\left(\frac{\partial^2 V}{\partial x_j x_i}\right)\eta_i\eta_j = \frac{1}{2}V_{ij}\eta_i\eta_j \tag{A.4}$$

Also the kinetic energy can be rewritten in term of η_i

$$T = \frac{1}{2}m_{ij}\dot{x}_i\dot{x}_j = \frac{1}{2}m_{ij}(\dot{x}_{0i} + \dot{\eta}_i)(\dot{x}_{0j} + \dot{\eta}_j) = \frac{1}{2}m_{ij}\dot{\eta}_i\dot{\eta}_j = \frac{1}{2}T_{ij}\dot{\eta}_i\dot{\eta}_j \tag{A.5}$$

This means that the Lagrangian is in the form

$$\mathcal{L} = T - V = \frac{1}{2}\left(T_{ij}\dot{\eta}_i\dot{\eta}_j - V_{ij}\eta_i\eta_j\right) \tag{A.6}$$

Using the following results

$$\begin{aligned} \frac{\partial \mathcal{L}}{\partial \eta_i} &= \frac{\partial}{\partial \eta_i}\left(\frac{1}{2}\left(T_{jk}\dot{\eta}_j\dot{\eta}_k - V_{jk}\eta_j\eta_k\right)\right) = -\frac{1}{2}V_{jk}\frac{\partial}{\partial \eta_i}(\eta_j\eta_k) \\ &= -\frac{1}{2}V_{jk}(\eta_j\delta_{ji} + \eta_k\delta_{ki}) = -\frac{1}{2}(V_{ik}\eta_k + V_{ji}\eta_k) \\ &= -\frac{1}{2}(V_{ij}\eta_j + V_{ij}\eta_j) = -V_{ij}\eta_j \end{aligned} \tag{A.7}$$

$$\begin{aligned}\frac{\partial \mathcal{L}}{\partial \dot\eta_i} &= \frac{\partial}{\partial \dot\eta_i}\left(\frac{1}{2}\left(T_{jk}\dot\eta_j\dot\eta_k - V_{jk}\eta_j\eta_k\right)\right) = -\frac{1}{2}T_{jk}\frac{\partial}{\partial \dot\eta_i}\left(\dot\eta_j\dot\eta_k\right) \\ &= -\frac{1}{2}T_{jk}\left(\dot\eta_j\delta_{ji} + \dot\eta_k\delta_{ki}\right) = -\frac{1}{2}\left(T_{ik}\dot\eta_k + T_{ji}\dot\eta_k\right) \\ &= -\frac{1}{2}\left(T_{ij}\dot\eta_j + T_{ij}\dot\eta_j\right) = -T_{ij}\dot\eta_j \end{aligned} \tag{A.8}$$

$$\frac{d}{dt}\left(T_{ij}\dot\eta_j\right) = T_{ij}\ddot\eta_j \tag{A.9}$$

since $V_{ij} = V_{ji}$ and $T_{ij} = T_{ji}$, the equation of motion respect to η_i are

$$\frac{d}{dt}\frac{\partial \mathcal{L}}{\partial \dot\eta_i} - \frac{\partial \mathcal{L}}{\partial \eta_i} = T_{ij}\ddot\eta_j + V_{ij}\eta_j = 0 \tag{A.10}$$

The solution of this equation is in the form $\eta_i = Ca_i e^{-i\omega t}$, with Ca_i the complex amplitude of η_i (C is a scale factor).

If we substitute this definition in (A.10) we obtain

$$V_{ij}a_j - \omega^2 T_{ij}a_j = 0 \tag{A.11}$$

these are N homogeneous linear equations in a_j that have non trivial solutions if the determinant is zero.

This means we have to compute

$$\begin{vmatrix} V_{11} - \omega^2 T_{11} & .... & V_{1N} - \omega^2 T_{1N} \\ ..... & .... & ..... \\ V_{N1} - \omega^2 T_{N1} & .... & V_{NN} - \omega^2 T_{NN} \end{vmatrix} = 0 \tag{A.12}$$

That is an algebraic equation of N-th order in ω^2. For each value of ω^2 we can solve a_j in (A.11). That means that (A.11) can be seen as an eigenvalue equation

$$\mathbf{Va} = \lambda \mathbf{Ta} \tag{A.13}$$

with $\mathbf{V} = V_{ij}, \mathbf{T} = T_{ij}$, $\lambda = \omega^2$ and $\mathbf{a}$ is the eigenvector associated to λ. Hence we can also write (A.4) and (A.5) in the matrix form

$$V = \frac{1}{2}\tilde{\eta}\mathbf{V}\eta \quad \text{and} \quad T = \frac{1}{2}\tilde{\dot\eta}\mathbf{T}\dot\eta \tag{A.14}$$

with

$$\eta = \begin{pmatrix} \eta_1 \\ ... \\ \eta_N \end{pmatrix} \text{ and } \tilde{\eta} = (\eta_1 \ \ ... \ \ \eta_N) \tag{A.15}$$

There is still an indetermination on a_{ij} that can be solved by putting $\tilde{\mathbf{a}}\mathbf{T}\mathbf{a} = \mathbf{1}$, which in matrix form is translated as

$$\tilde{\mathbf{A}}\mathbf{T}\mathbf{A} = \mathbf{1} \tag{A.16}$$

or

$$\tilde{\mathbf{A}}\mathbf{V}\mathbf{A} = \lambda \tag{A.17}$$

with $\mathbf{A} = a_{ij}$, the eigenvector matrix.

We have said before that $\eta_i = Ca_i e^{-i\omega t}$ is the solution of the equation of motion in (A.10), but specifically the complete solution is a superposition of the permitted frequencies, which means it is written as

$$\eta_i = C_k a_{ik} e^{-i\omega_k t} \tag{A.18}$$

that is simply a sum on the index k, which means that every η_i is the sum of harmonic oscillations with frequencies ω_k that satisfy (A.11).

Now we have the frequencies ω_k and the amplitude a_{ik}, we are just missing the scale factors C_k which will be given by

$$\eta(0) = \mathbf{A}Re\mathbf{C} \ \text{ or similarly } \ Re\mathbf{C} = \tilde{\mathbf{A}}\mathbf{T}\eta(0) \tag{A.19}$$

We can now obtain the normal variables by using the relation

$$\eta = \mathbf{A}\xi \ \text{ or } \ \xi = \tilde{\mathbf{A}}\mathbf{T}\eta \tag{A.20}$$

where ξ_k are the normal modes.

In this way the potential and kinetic energies become

$$V = \frac{1}{2}\tilde{\eta}\mathbf{V}\eta = \frac{1}{2}\widetilde{\mathbf{A}\xi}\mathbf{V}\mathbf{A}\xi = \frac{1}{2}\tilde{\xi}\tilde{A}\mathbf{V}\mathbf{A}\xi = \frac{1}{2}\tilde{\xi}\lambda\xi = \frac{1}{2}\omega_k^2\xi_k^2 \tag{A.21}$$

$$T = \frac{1}{2}\tilde{\dot{\eta}}\mathbf{T}\dot{\eta} = \frac{1}{2}\tilde{\dot{\xi}}\tilde{\mathbf{A}}\mathbf{T}\mathbf{A}\dot{\xi} = \frac{1}{2}\tilde{\dot{\xi}}\dot{\xi} = \frac{1}{2}\dot{\xi}_k^2 \tag{A.22}$$

where the relations (A.16) and (A.17) have been used.

Now both the matrices **V** and **T** are in diagonal form and their terms are all quadratic. The new Lagrangian is

$$\mathcal{L} = \frac{1}{2}(\dot{\xi}_k^2 - \omega_k^2\xi_k^2) \tag{A.23}$$

and the corresponding Hamiltonian

$$H = \frac{1}{2}(\dot{\xi}_k^2 + \omega_k^2\xi_k^2) \tag{A.24}$$

and both, as we said before, are in diagonal form, since they are the sum of diagonal matrices.

The equations of motion are now

$$\ddot{\xi}_k + \omega_k^2\xi_k^2 = 0 \tag{A.25}$$

whose solutions are

$$\xi_k = c_k e^{-i\omega_k t} \tag{A.26}$$

this means that every coordinate ξ_k is a periodic function in t corresponding to one *single* resonance frequency ω_k and all these variables are independent from each other.

A.2 2-Particle System

In this section we are going to illustrate the full procedure about how writing the Hamiltonian in normal modes starting from Cartesian, or generalized, coordinates.

Here the system is made by two particles with the same mass and elastic constant (the case we are dealing with in Chapter 2). The Hamiltonian is obviously written as in (2.21)

$$\begin{aligned} H &= \frac{1}{2}\sum_{i=0}^{2}\left[m\dot{x}_i^2 + k(x_{i+1}-x_i)^2\right] \\ &= \left[\frac{m}{2}\dot{x}_1^2 + \frac{m}{2}\dot{x}_2^2 + kx_1^2 + kx_2^2 - kx_1x_2 + \frac{1}{2}kL^2\right] \qquad \text{(A.27)} \end{aligned}$$

with $x_3 = L$ the total length of the chain, $x_0 = 0$ and $\dot{x}_0 = \dot{x}_3 = 0$ (fixed edges). We now make the following change of variables

$$x_1 = x_{01} + \eta_1 \qquad \text{(A.28)}$$

$$x_2 = x_{02} + \eta_2 \qquad \text{(A.29)}$$

with η_1 and η_2 the displacement from the equilibrium position of particle 1 and 2 and x_{01} and x_{02} their equilibrium position (in this case $x_{02} - x_{01} = L - x_{02} = a$).

The kinetic energy is

$$T = \frac{1}{2}m\dot{x}_1^2 + \frac{1}{2}m\dot{x}_2^2 = \frac{1}{2}m\dot{\eta}_1^2 + \frac{1}{2}m\dot{\eta}_2^2 = \frac{1}{2}\dot{\eta}^T\mathbf{T}\dot{\eta} \qquad \text{(A.30)}$$

because $\dot{x}_{01} = \dot{x}_{02} = 0$ and with

$$\mathbf{T} = \begin{pmatrix} m & 0 \\ 0 & m \end{pmatrix} \text{ and } \dot{\eta} = \begin{pmatrix} \dot{\eta}_1 \\ \dot{\eta}_2 \end{pmatrix} \text{ and } \dot{\eta} = (\dot{\eta}_1 \ \ \dot{\eta}_2) \qquad \text{(A.31)}$$

The potential energy is now

$$\begin{aligned} V &= \frac{1}{2}(x_1 - a)^2 + \frac{1}{2}(x_2 - x_1 - a)^2 + \frac{1}{2}(L - x_2 - a)^2 \\ &= \frac{1}{2}(x_{01} + \eta_1 - a)^2 + \frac{1}{2}(x_{02} + \eta_2 - x_{01} - \eta_1 - a)^2 \\ &+ \frac{1}{2}(L - x_{02} - \eta_2 - x_1 - a)^2 \\ &= \frac{1}{2}\left[2\eta_2^2 + 2\eta_1^2 - 2\eta_1\eta_2\right] = \frac{1}{2}\eta^T\mathbf{V}\eta \qquad \text{(A.32)} \end{aligned}$$

with

$$\mathbf{V} = k \begin{pmatrix} 2 & -1 \\ -1 & 2 \end{pmatrix} \quad \text{and } \eta = \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \quad \text{and } \eta = (\eta_1 \ \ \eta_2) \tag{A.33}$$

It is important to underline that, concerning the displacement from equilibrium, we are treating here $x_{01} = a$ (following the path of [30]) while in the analytical calculations in Chapter 2 $x_{01} = 0$. This is actually of no importance because the results for the kinetic and potential energy is going to be the same in the two cases.

We have to find now the eigenvalues of the secular equation as in (A.12)

$$\text{Det}\left(\mathbf{V} - \omega^2 \mathbf{T}\right) = 0 \quad \text{with} \quad \omega^2 = \lambda \tag{A.34}$$

$$\begin{vmatrix} 2k - \lambda m & -k \\ -k & 2k - \lambda m \end{vmatrix} = (2k - \lambda m)^2 - k^2 = 0 \tag{A.35}$$

whose result are

$$\lambda_1 = k/m = \omega_1^2 \quad \lambda_1 = 3k/m = \omega_2^2 \tag{A.36}$$

that brings to $\omega_1 = \sqrt{k/m}$ and $\omega_2 = \sqrt{3k/m}$, since the negative frequencies are ruled out.

Now we are getting the eigenvectors of each frequency starting from ω_1, that means we have to solve the following equation

$$(\mathbf{V} - \omega_1^2 \mathbf{T}) a_{i1} = 0 \tag{A.37}$$

that in matrix form is

$$\begin{pmatrix} 2k - \dfrac{k}{m} & -k \\ -k & 2k - \dfrac{k}{m} \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{21} \end{pmatrix} = \begin{pmatrix} k & -k \\ -k & k \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{21} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{A.38}$$

that brings to

$$(a_{11} \ \ a_{21}) \propto (1 \ \ 1) \tag{A.39}$$

For the normalization we can use $\tilde{a}_k \mathbf{T} \tilde{a}_k = 1$ (as in (A.16)) that in matrix form is

$$(a_{11} \quad a_{21}) \begin{pmatrix} m & 0 \\ 0 & m \end{pmatrix} \begin{pmatrix} a_{11} \\ a_{21} \end{pmatrix} = ma_{11}^2 + ma_{21}^2 = 2ma_{11}^2 = 1 \tag{A.40}$$

which means

$$a_{11} = \frac{1}{\sqrt{2m}} \tag{A.41}$$

In conclusion we have

$$a_{i1} = \frac{1}{\sqrt{2m}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \tag{A.42}$$

For the second eigenvalue $\omega_2^2 = \frac{3k}{m}$ we follow the same procedure and we have

$$a_{i2} = \frac{1}{\sqrt{2m}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \tag{A.43}$$

The matrix A of the eigenvectors is then

$$A = \begin{pmatrix} 1/\sqrt{2m} & 1/\sqrt{2m} \\ 1/\sqrt{2m} & -1/\sqrt{2m} \end{pmatrix} \tag{A.44}$$

We can now write η_i (A.18)

$$\eta_1 = c_1 a_{11} e^{-i\omega_1 t} + c_2 a_{12} e^{-i\omega_2 t} = c_1 \frac{1}{\sqrt{2m}} e^{-i\sqrt{\frac{k}{m}}t} + c_2 \frac{1}{\sqrt{2m}} e^{-i\sqrt{\frac{3k}{m}}t} \tag{A.45}$$

$$\eta_2 = c_1 a_{21} e^{-i\omega_1 t} + c_2 a_{22} e^{-i\omega_2 t} = c_1 \frac{1}{\sqrt{2m}} e^{-i\sqrt{\frac{k}{m}}t} - c_2 \frac{1}{\sqrt{2m}} e^{-i\sqrt{\frac{3k}{m}}t} \tag{A.46}$$

we can finally obtain the normal modes ξ_i by using the relation in (A.20) $\xi = \tilde{\mathbf{A}}\mathbf{T}\eta$. The matrix $\tilde{\mathbf{A}}\mathbf{T}$ is

$$\tilde{\mathbf{A}}\mathbf{T} = \begin{pmatrix} 1/\sqrt{2m} & 1/\sqrt{2m} \\ 1/\sqrt{2m} & -1/\sqrt{2m} \end{pmatrix} \begin{pmatrix} m & 0 \\ 0 & m \end{pmatrix} = \frac{1}{\sqrt{2m}} \begin{pmatrix} m & m \\ m & -m \end{pmatrix} \tag{A.47}$$

so that our solutions are

$$\begin{pmatrix} \xi_1 \\ \xi_2 \end{pmatrix} = \frac{1}{\sqrt{2m}} \begin{pmatrix} m & m \\ m & -m \end{pmatrix} \begin{pmatrix} \eta_1 \\ \eta_2 \end{pmatrix} \tag{A.48}$$

and we explicitly obtain

$$\xi_1 = c_1 e^{-i\omega_1 t} \tag{A.49}$$

$$\xi_2 = c_2 e^{-i\omega_2 t} \tag{A.50}$$

with c_1 and c_2 given by the initial conditions (in Chapter 2 $c_1 = c_2 = 1$). These are the variables that we are using in the Hamiltonian in (2.8) where $\omega_1 = \sqrt{k/m}$, $\omega_2 = \sqrt{3k/m}$ and $\tilde{x}_i = \xi_i$ and $\tilde{v}_i = \dot{\xi}_i$ for $i = 1, 2$.

Appendix B

Numerical Codes

In this Appendix we are illustrating the complete codes that have been used for the numerical simulations. We separate the two cases referring to the harmonic and the FPU potential since some changes are needed to pass from one scenario to the other one. All the codes are written in Fortran90.

B.1 Harmonic Potential

As explained in Chapter 4, the simulation is divided into four steps. The first is to build Σ^{-1}, the inverse of the covariance matrix, using (4.9), basically all the quadratic terms in $-\beta H(x, v) - \gamma J(x, v)$, the argument of the exponential in the probability density function in (4.6).

The code is written with allocatable arrays, so that the number of particles in the chain is not fixed but it can be changed every time the simulation is run. Hence, the first program builds this matrix, where also the various parameters that describe the system, like the mass, the elastic coupling or the intensity of the distortion, can be modified.

```
! the different parameters of the system are set
module parametri

real,parameter:: m=1.
real,parameter:: k=1.
real, parameter::beta=1.
real, parameter::a0=1.
real, parameter::g=1.

end module parametri

!main program
program matrix

use parametri
implicit none

integer :: i1, i2, j1, j2, k1, k2, n
real, allocatable, dimension(:,:) :: H, J, S, U

open (unit=1, file="matrice.dat")
open (unit=2, file="numero_particelle.dat")

! the number of particles in the chain is set
write(*,*) "Numero di particelle?"
read(*,*) n
write(2,*) n
allocate (H(2*n,2*n),J(2*n,2*n),U(2*n,2*n),S(2*n,2*n))

do i1=1,2*n

      do i2=1,2*n

if (i1<n+1 .and. i2<n+1 .and. i1==i2) then
H(i1,i2)=2*beta*k
else if (i1<n+1 .and. i2<n+1 .and. i1==i2+1 ) then
H(i1,i2)=-1*beta*k
else if (i1<n+1 .and. i2<n+1 .and. i1+1==i2 ) then
H(i1,i2)=-1*beta*k
else if (i1>n .and. i2>n .and. i1==i2) then
```

```
            H(i1,i2)=1*beta*m
            else
            H(i1,i2)=0
            end if

        end do

      end do

do j1=1,2*n

do j2=1,2*n

    if (j1==j2+n+1) then
J(j1,j2)=(1/2.)*(g*k*a0)
else if (j2==j1+n+1) then
J(j1,j2)=(1/2.)*(g*k*a0)
else if (j2>n .and. j2<2*n .and. j1==j2-n+1 ) then
J(j1,j2)=-(1/2.)*(g*k*a0)
else if (j1>n .and. j1<2*n .and. j2==j1-n+1  ) then
J(j1,j2)=-(1/2.)*(g*k*a0)
            else
            J(j1,j2)=0
            end if

        end do

      end do

S=H+J

! here the final matrix with the quadratic terms in H+J is written to a file

write(1,*) S

close(1)
close(2)

end program matrix
```

The aim of the second code is to get the average μ we need to build our random number distribution in (4.6), using the relation (4.9).

```
! the different parameters of the system are set
module parametri

real,parameter:: m=1.
real,parameter:: k=1.
real, parameter::beta=1.
real, parameter::a0=1.
real, parameter::g=1.

end module parametri

program media
use parametri
implicit none

real, allocatable, dimension(:,:) :: a
real, allocatable, dimension(:) :: mu, b
integer :: L, i, n

open(1,file="numero_particelle.dat",status="old",action="read")
open(2,file="matrice.dat",status="old",action="read")
open(3,file="media.dat")

read(1,*) n
allocate (a(2*n,2*n),mu(2*n),b(2*n))

L=n+1

! the equation in (4.8) for the average is built
b=0.0
b(n)=beta*k*L
b(2*n)=g*k*a0*L/2.


read(2,*) a
mu(2*n)=b(2*n)/a(2*n,2*n)
```

```
!here the equation is solved
call gauss (n,a,b)

call triangsuperiore (n,a,b,mu)

!the average is written to a file
write(3,*) mu

close(1)
close(2)
close(3)

end program media

!subroutine used to solve matrix equation AX=B
subroutine gauss (n,a,b)
implicit none

integer :: n,k,i,err
real :: a(1:2*n,1:2*n), b(1:2*n), aux

  do k=1,2*n-1
call pivot()
err=k
if (ABS(a(k,k))<1.E-09)   return

do i = k+1,2*n
            aux = a(i,k)/a(k,k)
            a(i,k)=0
            a(i,k+1:2*n) = a(i,k+1:2*n) - aux*a(k,k+1:2*n)
            b(i)=b(i)-aux*b(k)
end do

  end do

err=0
if (ABS(a(2*n,2*n))<1.E-09) err=2*n


contains
```

```
  subroutine pivot()
  integer :: iipiv(1)
  real :: apiv(k:2*n), bpiv

  iipiv = MAXLOC (ABS(a(k:2*n,k))) +k-1
     if (iipiv(1) /= k) then
          apiv = a(k,k:2*n)
          bpiv = b(k)

          a(k,k:2*n) = a(iipiv(1),k:2*n)
          b(k) = b(iipiv(1))

          a(iipiv(1),k:2*n)=apiv
          b(iipiv(1))=bpiv
      end if

  end subroutine pivot

end subroutine gauss

!subroutine used to transform the initial matrix
!in a upper triangular matrix

subroutine triangsuperiore (n,a,b,mu)

implicit none
integer :: n, i, k
real :: a(2*n,2*n),b(2*n),mu(2*n),err

do i=1,2*n

if(ABS(a(i,i))<1.E-9) then
err=i
return
end if

end do

err=0

mu(2*n)=b(2*n)/a(2*n,2*n)
```

```
do k=2*n-1,1,-1
        mu(k)=b(k)
        mu(k)=b(k)-DOT_PRODUCT(a(k,k+1:2*n),mu(k+1:2*n))
        mu(k)=mu(k)/a(k,k)
end do

end subroutine triangsuperiore
```

After the average is gotten, we still need the covariance matrix Σ for the distribution of the initial random numbers. Σ is the inverse of the matrix that contains the quadratic terms of $-\beta H(x,v) - \gamma J(x,v)$, but some constants. Hence this code considers the matrix printed in the first code and gives as an output the inverse with the suitable constants as illustrated in (4.9).

```
program elim_gauss

implicit none
integer :: n, k, i, err, ipiv, j
real, allocatable :: a(:,:), ao(:,:), b(:), e(:), inv(:,:), x(:), sol(:)


open(1,file="numero_particelle.dat",status="old",action="read")
open(2,file="matrice.dat",status="old",action="read")
open(3,file="inversa.dat")

read (1,*) n

n=2*n

allocate (a(1:n,1:n),ao(1:n,1:n),b(1:n),e(1:n),inv(1:n,1:n),x(1:n),sol(1:n))
read (2,*) ao
write(*,*),' Vuoi usare il pivoting ? ( si = 1 )' ; READ*,ipiv

do j=1,n
a=ao
e=0
```

```
e(j)=1
call gauss(n,a,e,ipiv,err)
if (err /=0) PRINT*,’ gauss err’,j
call triangsuperiore(n,a,e,x,err)
if (err /=0) PRINT*,’ ts err’,j
inv(1:n,j)=x(1:n)
end do

! the covariance matrix is printed to a file
if (err==0) then
do k=1,n
write(3,*) inv(k,1:n)
    end do

end if

if (err /=0) write(*,*),’La matrice e’’ singolare, elemento(’, err,’) nullo’

close(1)
close(2)
close(3)

end program elim_gauss

! subroutine the solves the matrix equation in the form AX=B

subroutine gauss (n,a,b,ipiv,err)

implicit none

integer :: n, k, i, err, ipiv
real :: a(1:n,1:n), b(1:n), aux

  do k=1,n-1
      if (ipiv==1) call pivot()
      err=k
       if (ABS(a(k,k))<1.E-09)   return
         do i = k+1,n
            aux = a(i,k)/a(k,k)
            a(i,k)=0
            a(i,k+1:n) = a(i,k+1:n) - aux*a(k,k+1:n)
```

```
            b(i)=b(i)-aux*b(k)
         end do
  end do

err=0
if (ABS(a(n,n))<1.E-09) err=n

contains

  subroutine pivot()
  integer :: iipiv(1)
  real :: apiv(k:n), bpiv

  iipiv = MAXLOC (ABS(a(k:n,k))) +k-1
     if (iipiv(1) /= k) then
          apiv = a(k,k:n)
          bpiv = b(k)

          a(k,k:n) = a(iipiv(1),k:n)
          b(k) = b(iipiv(1))

          a(iipiv(1),k:n)=apiv
          b(iipiv(1))=bpiv
      end if

  end subroutine pivot

end subroutine gauss


!subroutine used to transform the initial matrix
!in a upper triangular matrix

subroutine triangsuperiore (n,a,b,sol,err)

implicit none

integer :: n, err, i, k
real :: a(n,n), b(n), sol(n)

do i=1,n
```

```
if(ABS(a(i,i))<1.E-9) then
err=i
return
end if
end do

err=0


sol(n)=b(n)/a(n,n)
do k=n-1,1,-1
        sol(k)=b(k)
        sol(k)=b(k)-DOT_PRODUCT(a(k,k+1:n),sol(k+1:n))
        sol(k)=sol(k)/a(k,k)
end do

end subroutine triangsuperiore
```

Finally, having Σ and μ, hence the distribution of the random numbers, we can run the Monte Carlo simulation to compute the different observables of the system.

```
Module UniformDev
  Interface
     Function Random ()
       Implicit None
       Real(8) :: Random
     End Function Random
  End Interface
End Module UniformDev

Module GaussianDev
  Interface
     Function GasDev(c,w)
       Use UniformDev
       Implicit None
       Real(8), Intent(In) :: c,w
       Real(8)             :: GasDev
     End Function GasDev
```

```
  End Interface
End Module GaussianDev

! Uniform Random Generator.

Function Random ()
  Implicit None

  Real(8) :: Random
  Real(8) :: r

  Call Random_Number(r)
  Random = r

End Function Random

! Gaussian Random Generator (It uses the function Random)
! P(x)dx = (2*pi*w)^(-1/2) * exp ( -(1/(2*w))*(x-c)^2 ) dx
! Then the distribution is normalized Gaussian distribution centered
! around "c" and with a variance <x^2> - <x>^2 = w.

Function GasDev(c,w)
  Use UniformDev
  Implicit None

  Real(8), Intent(In) :: c, w
  Real(8)             :: GasDev
  Real(8)             :: v1, v2, rsq, fac

  rsq = 0.0
  do
     if ((rsq < 1.0_8) .and. (rsq /= 0.0_8)) exit
     v1 = 2.0_8*Random() - 1.0_8
     v2 = 2.0_8*Random() - 1.0_8
     rsq = v1*v1 + v2*v2
  end do

  fac = sqrt(-2.0_8*w*log(rsq)/rsq)
  GasDev = v2*fac + c

end function GasDev
```

```
program main

    Use GaussianDev
Use UniformDev

implicit none
    integer :: enne=1000000
    integer :: i, j, k1, k2, n, l
real,allocatable,dimension(:) :: mu, x, f, f2, y, var
    real,allocatable,dimension(:,:) :: sigma, inv
    character(3) :: sdim
    character(40) :: sf

    open(1,file="numero_particelle.dat",status="old",action="read")
open(2,file="media.dat",status="old",action="read")
open(3,file="inversa.dat",status="old",action="read")
    open(4,file="x_medio.dat")
    open(5,file="v_medio.dat")
    open(7,file="x_quadro.dat")
open(8,file="x_varianza.dat")

! values of the average and the covariance matrix
read(1,*) n
allocate(mu(2*n),x(2*n),y(2*n),var(2*n),sigma(2*n,2*n),f(2*n),f2(2*n))

f= 0.0
    f2 = 0.0

    read(2,*) mu
    read(3,*) sigma

  !-- sigma corresponds to -2 times the covariance matrix.
  !-- We first perform the Cholesky decomposition

 Call Cholesky(sigma,2*n)

do i = 1,enne  !-- enne realizations

     !-- First we generate a vector y whose components are i.i.d.
     !random variables with zero mean and unit variance.
```

```
do k1 = 1,2*n
y(k1) = real(GasDev(0.0_8,1.0_8))
        end do

     !-- Now we generate a vector x which is a random deviate of the multivariate
     !-- measure with mean mu and covariance matrix sigma
     x = 0.0
do k1 = 1,2*n
do k2 = 1,k1
x(k1) = x(k1) + sigma(k1,k2)*y(k2)
end do
end do

x = x + mu
f = f+x
f2 = f2+x**2

end do

! we take the average of f and f2
  f = f/real(enne)
  f2 = f2/real(enne)

! print the observables <x>, <x^2>, and <v>

! observable <x>
     do l=1,n-1
     write (4,*) l, (f(l+1)-f(l))
     end do

! observable <v>
do l=n+1, 2*n
     write (5,*) l, f(l)
     end do

! observable <x^2>
    do l=1,n
    write (7,*) l, f2(l)
    end do

! variance of <x>
```

```
do l=1,n
    write (8,*) l, f2(l)-f(l)**2
    end do

close(1)
close(2)
close(3)
close(4)
close(5)
close(7)
close(8)

end program main

subroutine Cholesky(A,n)
  Implicit None

  integer, intent(In) :: n      ! dimension of the matrix (for us 2N)
  real, intent(InOut) :: A(n,n) ! matrix to be decomposed
  integer :: i,j

  do j = 1,n
    !-- perform diagonal component
    A(j,j) = sqrt(A(j,j) - dot_product(A(j,1:j-1),A(j,1:j-1)))
    !-- perform off-diagonal component
    If (j < n) Then
       A(j+1:n,j) = (A(j+1:n,j) - matmul(A(j+1:n,1:j-1),A(j,1:j-1)))/A(j,j)
    end if
  end do
  do i = 1,n
     do j = 1,n
        if (j > i) A(i,j) = 0.0
     end do
  end do

end subroutine Cholesky
```

B.2 FPU Potential

The logical structure of the code for the FPU potential is the same as the previous one. Anyway, some changes are needed. The covariance matrix and the average of the distribution of the random numbers have some additional terms, due to the fact the the argument in the exponential of (6.1) has now more linear and quadratic terms. This is the first difference between the two potentials. Below there is the code to build the matrix Σ^{-1}, with these additional terms on the n-the and $2n$-th variables.

```
! the different parameters of the system are set
module parametri

real,parameter:: m=1.
real,parameter:: k=1.
real, parameter::beta=1.
real, parameter::a0=1.
real, parameter::g=1.

end module parametri

!main program
program matrix

use parametri
implicit none

integer :: i1, i2, j1, j2, k1, k2, n
real, allocatable, dimension(:,:) :: H, J, S, U

open (unit=1, file="matrice.dat")
open (unit=2, file="numero_particelle.dat")

! the number of particles in the chain is set
write(*,*) "Numero di particelle?"
read(*,*) n
write(2,*) n
```

```
allocate (H(2*n,2*n),J(2*n,2*n),U(2*n,2*n),S(2*n,2*n))

do i1=1,2*n

      do i2=1,2*n

if (i1<n+1 .and. i2<n+1 .and. i1==i2) then
H(i1,i2)=2*beta*k
!here there is the difference respect to the harmonic potential case
else if (i1==n .and. i2==n) then
H(i1,i2)=2*beta*(k+k3*L)
else if (i1<n+1 .and. i2<n+1 .and. i1==i2+1 ) then
H(i1,i2)=-1*beta*k
else if (i1<n+1 .and. i2<n+1 .and. i1+1==i2 ) then
H(i1,i2)=-1*beta*k
else if (i1>n .and. i2>n .and. i1==i2) then
            H(i1,i2)=1*beta*m
            else
            H(i1,i2)=0
            end if

        end do

      end do

do j1=1,2*n

do j2=1,2*n

    if (j1==j2+n+1) then
J(j1,j2)=(1/2.)*(g*k*a0)
else if (j2==j1+n+1) then
J(j1,j2)=(1/2.)*(g*k*a0)
else if (j2>n .and. j2<2*n .and. j1==j2-n+1 ) then
J(j1,j2)=-(1/2.)*(g*k*a0)
else if (j1>n .and. j1<2*n .and. j2==j1-n+1  ) then
J(j1,j2)=-(1/2.)*(g*k*a0)
            else
            J(j1,j2)=0
            end if
```

```
        end do

      end do

S=H+J

! here the final matrix H+J is written to a file

write(1,*) S

close(1)
close(2)

end program matrix
```

As a second step we build the average μ we need for the distribution (6.2): as before we have some additional terms only on the n-th and $2n$-th variables. The third code used to get the inverse of the matrix Σ^{-1} is not written, since it is the same as in the harmonic case.

```
! the different parameters of the system are set
module parametri

real,parameter:: m=1.
real,parameter:: k=1.
real, parameter::beta=1.
real, parameter::a0=1.
real, parameter::g=1.

end module parametri

program media
use parametri
implicit none

real, allocatable, dimension(:,:) :: a
real, allocatable, dimension(:) :: mu, b
integer :: L, i, n
```

```
open(1,file="numero_particelle.dat",status="old",action="read")
open(2,file="matrice.dat",status="old",action="read")
open(3,file="media.dat")

read(1,*) n
allocate (a(2*n,2*n),mu(2*n),b(2*n))

L=n+1

! the equation in (4.8) for the average is built
b=0.0
!here there is the difference respect to the harmonic potential case
b(n)=beta*k*L+beta*k3*L**2
b(2*n)=g*k*a0*L/2.


read(2,*) a
mu(2*n)=b(2*n)/a(2*n,2*n)

!here the equation is solved
call gauss (n,a,b)

call triangsuperiore (n,a,b,mu)

!the average is written to a file
write(3,*) mu

close(1)
close(2)
close(3)

end program media

!subroutine used to solve matrix equation
subroutine gauss (n,a,b)
implicit none

integer :: n,k,i,err
real :: a(1:2*n,1:2*n), b(1:2*n), aux
```

```
  do k=1,2*n-1
call pivot()
err=k
if (ABS(a(k,k))<1.E-09)   return

do i = k+1,2*n
            aux = a(i,k)/a(k,k)
            a(i,k)=0
            a(i,k+1:2*n) = a(i,k+1:2*n) - aux*a(k,k+1:2*n)
            b(i)=b(i)-aux*b(k)
end do

  end do

err=0
if (ABS(a(2*n,2*n))<1.E-09) err=2*n


contains

  subroutine pivot()
  integer :: iipiv(1)
  real :: apiv(k:2*n), bpiv

  iipiv = MAXLOC (ABS(a(k:2*n,k))) +k-1
     if (iipiv(1) /= k) then
          apiv = a(k,k:2*n)
          bpiv = b(k)

          a(k,k:2*n) = a(iipiv(1),k:2*n)
          b(k) = b(iipiv(1))

          a(iipiv(1),k:2*n)=apiv
          b(iipiv(1))=bpiv
      end if

  end subroutine pivot

end subroutine gauss

!subroutine used to transform the initial matrix
```

```
!in a upper triangular matrix

subroutine triangsuperiore (n,a,b,mu)

implicit none
integer :: n, i, k
real :: a(2*n,2*n),b(2*n),mu(2*n),err

do i=1,2*n

if(ABS(a(i,i))<1.E-9) then
err=i
return
end if

end do

err=0

mu(2*n)=b(2*n)/a(2*n,2*n)

do k=2*n-1,1,-1
        mu(k)=b(k)
        mu(k)=b(k)-DOT_PRODUCT(a(k,k+1:2*n),mu(k+1:2*n))
        mu(k)=mu(k)/a(k,k)
end do

end subroutine triangsuperiore
```

Finally, as before, we have the covariance matrix Σ and the average μ and we can run the Monte Carlo simulation. Also here, there are some difference respect to the previous case. Now the computation is not only on a generic observable A but also on some cubic terms in the exponent (6.7), hence the function we are evaluating is the observable times a sum of exponential cubic terms. Observing the formula in (6.7), we are evaluating two function and then we are getting their ratio: in this way we can obtain the original value

$\langle A \rangle$ with the corresponding measure of the ensemble.

Also, in this case a change in the memory of some variables is needed since the Monte Carlo works on the sum of a function evaluated N times: here there are some cubic terms in the exponential and the value of the sum increases dramatically fast. Hence, the variables that evaluate these sum are changed from variable of kind 8 to variable of kind 10.

Moreover, we have seen in Chapter 5 that the space variables need to have a restricted domain to ensure the convergence of the partition function: this is translated in the following code by rejecting all the random vectors whose values of the space coordinates are not included in the interval $[0, L]$, with L the length of the chain.

```
module parametri
real,parameter:: m=1.
real,parameter:: k=1.
real, parameter::beta=1.
real, parameter::a0=1.
real, parameter::g=1.
real, parameter::k3=1.
end module parametri

Module UniformDev
  Interface
     Function Random ()
     Implicit None
     Real(8) :: Random
     End Function Random
  End Interface
End Module UniformDev

Module GaussianDev
  Interface
     Function GasDev(c,w)
     Use UniformDev
     Implicit None
```

```
     Real(8), Intent(In) :: c,w
     Real(8)             :: GasDev
     End Function GasDev
  End Interface
End Module GaussianDev

! F90 Uniform Random Generator

Function Random ()
  Implicit None

  Real(8) :: Random
  Real(8) :: r

  Call Random_Number(r)
  Random = r

End Function Random

! Gaussian Random Generator (It uses the function Random)
! P(x)dx = (2*pi*w)^(-1/2) * exp ( -(1/(2*w))*(x-c)^2 ) dx
!
! Then the distribution is normalized Gaussian distribution centered
! around "c" and with a variance <x^2> - <x>^2 = w.

Function GasDev(c,w)
  Use UniformDev
  Implicit None

  Real(8), Intent(In) :: c,w
  Real(8)             :: GasDev
  Real(8)             :: v1,v2,rsq,fac

  rsq = 0.0
  do
     if ((rsq < 1.0_8) .and. (rsq /= 0.0_8)) exit
     v1 = 2.0_8*Random() - 1.0_8
     v2 = 2.0_8*Random() - 1.0_8
     rsq = v1*v1 + v2*v2
  end do
  fac = sqrt(-2.0_8*w*log(rsq)/rsq)
```

```
  GasDev = v2*fac + c

end function GasDev

program main
use parametri
    use GaussianDev
use UniformDev

    implicit none
    integer:: enne=100000
    integer :: i,k1,k2,n,l, emme, p, elle
real(8),allocatable,dimension(:) :: mu,x,y,var
    real(10),allocatable,dimension(:) ::f, f2
    real(10)::f_new2,f_new
    real(8),allocatable,dimension(:,:)::sigma


    open(1,file="numero_particelle.dat",status="old",action="read")
open(2,file="media.dat",status="old",action="read")
open(3,file="inversa.dat",status="old",action="read")
    open(4,file="x_medio.dat")
    open(5,file="v_medio.dat")
    open(7,file="x_quadro.dat")
open(8,file="x_varianza.dat")

      !values of the average and of the covariance matrix

read(1,*) n
allocate(mu(2*n),x(2*n),y(2*n),var(2*n),sigma(2*n,2*n),f(2*n),f2(2*n))

     f= 0.0
     f2 = 0.0
     f_new2=0.0

     read(2,*) mu
     read(3,*) sigma

  !-- sigma corresponds to -2 times the covariance matrix.
  !-- We first perform the Cholesky decomposition
  Call Cholesky(sigma,2*n)
```

```
i=0
do while (i <= enne)  !-- enne realizations
!-- First we generate a vector y whose components are i.i.d.
!random variables with zero mean and unit variance.

do k1 = 1,2*n
        y(k1) = real(GasDev(0.0_8,1.0_8))
end do

     !-- Now we generate a vector x which is a random deviate of the
     !multivariate measure with mean mu and covariance matrix sigma

     x = 0.0
     do k1 = 1,2*n
        do k2 = 1,k1
           x(k1) = x(k1) + sigma(k1,k2)*y(k2)
        end do
     end do

x = x + mu

emme=0

    do p=1,n

if ((x(p)<0) .OR. (x(p)>elle)) then
        emme=emme+1

        end if

    end do

        if (emme>=1) cycle
        i=i+1

f_new= 0.0

do l=1,n-1
f_new = f_new + x(l)*x(l+1)**2-x(l)**2*x(l+1)
end do
```

```
f_new2 = f_new2 + 2.718**(beta*k3*f_new)
f=f+x*2.718**(beta*k3*f_new)
f2 = f2+x**2

end do

  f = f/real(enne)
  f_new2 = f_new2/real(enne)
  f2 = f2/real(enne)


! print the observables <x>, <x^2>, and <v>
! observable <x>
     do l=1,n-1
     write (4,*) l, (f(l+1)-f(l))/f_new2
     end do

! observable <v>
do l=n+1, 2*n
     write (5,*) l, f(l)/f_new2
     end do

! observable <x^2>
    do l=1,n
    write (7,*) l, f2(l)/f_new2
    end do

! variance of <x>
do l=1,n
    write (8,*) l, f2(l)/f_new2-(f(l)/f_new2)**2
    end do

close(1)
close(2)
close(3)
close(4)
close(5)
close(7)
close(8)
```

```
end program main


Subroutine Cholesky(A,n)
  Implicit None

  Integer, Intent(In) :: n      ! dimension of the matrix (for us 2N)
  Real(8), Intent(InOut) :: A(n,n) ! matrix to be decomposed
  Integer :: i,j

  Do j = 1,n
    !-- perform diagonal component
    A(j,j) = sqrt(A(j,j) - dot_product(A(j,1:j-1),A(j,1:j-1)))
    !-- perform off-diagonal component
    If (j < n) Then
       A(j+1:n,j) = (A(j+1:n,j) - matmul(A(j+1:n,1:j-1),A(j,1:j-1)))/A(j,j)
    End If
  End Do
  Do i = 1,n
     Do j = 1,n
        If (j > i) A(i,j) = 0.0
     End Do
  End Do

End Subroutine Cholesky
```

Appendix C

Journal Papers

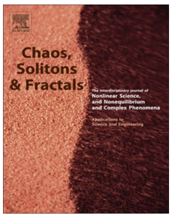
Chaos, Solitons & Fractals 64 (2014) 2–15

Contents lists available at ScienceDirect

Chaos, Solitons & Fractals

Nonlinear Science, and Nonequilibrium and Complex Phenomena

journal homepage: www.elsevier.com/locate/chaos



Focus on some nonequilibrium issues

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ABSTRACT

A mathematical framework for the physics of nonequilibrium phenomena is gradually being developed. This review is meant to shed light on some aspects of response theory, on the theory of Fluctuation Relations, on the so-called *t-mixing* condition, and on the use of large deviation techniques in the description of stochastic diffusion processes.

1. Introduction

Statistical Mechanics provides a mathematical formalism to bridge different scales of investigation of natural phenomena: (a) the microscopic scale, concerning the statistical or collective behaviour of large assemblies of atoms and molecules, approached e.g. in terms of statistical ensembles; (b) the mesoscopic scale, commonly described by the Boltzmann equation and its variations, or by more general and abstract stochastic processes; (c) and the macroscopic level, by and large the realm of fluid dynamics and Irreversible Thermodynamics which consider matter as a continuum.

Equilibrium phenomena have been investigated and understood much more thoroughly than non-equilibrium ones. At present, the theory may be considered complete, for what concerns the microscopic foundations of equilibrium thermodynamics, including the theory of phase transitions and critical phenomena. Differently, in spite of its celebrated history and of the countless and deep results obtained so far, Statistical Mechanics has not produced yet a comprehensive theoretical framework for non-equilibrium phenomena. These, indeed, are much more numerous, diverse and complex than equilibrium phenomena.

Nevertheless, problems posed, in particular, by the modern bio- and nano-technologies, have turned the attention of a large fraction of the Statistical Mechanics community towards the non-equilibrium phenomena. This has been possible also thanks to the progress of dynamical systems theory, which becomes necessary when the classical hypotheses of local equilibrium or kinetic theory [1] fail, as well as in describing macroscopic chaotic phenomena such as those of turbulence.[1] Indeed, in equilibrium there is no need to deal with the microscopic dynamics equations of motion, because the classical ensembles have been proven by experience to accurately capture the statistics for the macroscopic quantities and their fluctuations. On the contrary, the classical ensembles do not properly describe systems which are not in equilibrium, in which finite size effects and the persistence of space and time correlations may play a crucial role. Therefore, new hypotheses and novel approaches are required to describe these systems; in particular, understanding the dynamics of the microscopic constituents seems to be unavoidable to shed light even on the properties of stationary states.

As a matter of fact, the study of the macroscopic dynamics of dissipative particle systems, such as those of nonequilibrium molecular dynamics, has produced a number of results of direct interest in nonequilibrium statistical mechanics, including relations between transport coefficients and

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[1] Which take place in local equilibrium.

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Lyapunov exponents, which are presently part of a rather satisfactory theory of nonequilibrium liquids.

Twenty years ago, the first fluctuation relation for reversible deterministic dynamics was proposed, and remains one of the few exact and microscopic results for nonequilibrium systems. This led to new response formulae, which generalize the classical response theory to states far from the equilibrium, and to large perturbations of interest, e.g. in climate studies. Interestingly, various results obtained within the deterministic framework coincide with those obtained within the stochastic framework, which is reassuring, because in many situations the two frameworks aim at describing the same phenomenon.

Investigations of Fourier's law of heat conduction have continued along these dynamical lines since the early days of molecular dynamics and the Fermi–Pasta–Ulam problem, and today they have gained momentum thanks to the discovery of anomalies in the transport of matter, energy, charge etc. at the nanometric scales, which is of interest to bio- and nano-technology.

Dynamics and stochastics together may thus advance our understanding of the fundamental principles which are believed to be common to the incredibly wide spectrum of nonequilibrium phenomena, which ranges from microscopic to macroscopic scales and includes hydrodynamics and turbulence, biology, atmospheric physics, granular matter, nanotechnology, etc.

The wealth of techniques developed to tackle the problems of nonequilibrium physics can also be considered as a theoretical playground for many questions of foundational nature, such as determinism, chaos and randomness, or emergence and complexity, which find in the problem of irreversibility one of their earliest examples.

In this paper, we provide a review of some of the cornerstones of nonequilibrium Statistical Mechanics in order to clarify the corresponding physical mechanisms. This work is structured as follows.

In Section 2 we analyze the evolution of probability distributions, through the prism of Dynamical Systems theory.

In Section 3, we address the theory of linear response, whose origin can be traced back to the pioneering work of Kubo [2].

Section 4 focuses on the Onsager–Machlup theory, which concerns the regime of *small* fluctuations around equilibrium.

In Section 5, we review the theory of Fluctuation Relations.

Section 6 is devoted to the analysis of the *t-mixing* condition.

Section 7 presents some results concerning the use of large deviations techniques in stochastic diffusion processes.

Conclusions are drawn in Section 8.

2. Evolution of probability distributions

This section recalls basic notions of dynamical systems theory, introducing our notation. Consider a dynamical system defined by an evolution equation on a phase space $\mathcal{M}$:

$$\dot{\Gamma} = F(\Gamma), \quad \Gamma \in \mathcal{M} \tag{1}$$

whose trajectories for each initial condition Γ are given by $\{S^t\Gamma\}_{t\in\mathbb{R}}$, where S^t is the operator that moves Γ to its position after a time t (e.g. $S^0\Gamma = \Gamma$). We will consider time reversal invariant dynamics, i.e. dynamics obeying

$$IS^t\Gamma = S^{-t}I\Gamma, \quad \forall\Gamma \in \mathcal{M} \tag{2}$$

holds, where the linear operator $I : \mathcal{M} \to \mathcal{M}$ is an involution (I^2 =identity) representing a time reversal operation[2]. Furthermore, we will consider evolutions such that $\{S^t\}_{t\in\mathbb{R}}$ satisfies the group property $S^tS^s = S^{t+s}$. The time averages of a phase variable $\phi : \mathcal{M} \to \mathbb{R}$, along a trajectory starting at Γ, will be denoted by:

$$\overline{\phi}(\Gamma) = \lim_{t\to\infty}\frac{1}{t}\int_0^t \phi(S^s\Gamma)\,\mathrm{d}s \tag{3}$$

If the dynamics represents a thermodynamic system, in which Γ is a single microscopic phase, the time average should not depend on this phase, and could be obtained as a phase space average, with respect to a given probability distribution μ[3]:

$$\overline{\phi}(\Gamma) = \int_{\mathcal{M}} \phi(X)\mathrm{d}\mu(X) = \langle\phi\rangle_\mu, \quad \text{for } \mu\text{-almost every } \Gamma \in \mathcal{M} \tag{4}$$

This is the case if the dynamical system $(S, \mathcal{M}, \mu)$ is ergodic (cf. Section 2.1), which is a very strong property, not verified by most of the systems of physical interest. It can be however safely assumed to hold very often, because physics is often concerned with a small set of observables and with systems made of exceedingly large numbers of particles, c.f. [3].

Once $\mathcal{M}$ is endowed with a probability distribution $\mu_0, \mu_0(\mathcal{M}) = 1$ and $\mu_0(E) \geqslant 0$ for all allowed events $E \subset \mathcal{M}$, the dynamics in $\mathcal{M}$ may be used to induce an evolution in the space of probabilities. One may assume that the subsets of the phase space have a certain probability, which they carry along where the dynamics moves them. As a consequence, the probability distribution on $\mathcal{M}$ changes in time, and one may introduce a set of distributions $\{\mu_t\}_{t\in\mathbb{R}}$ as follows:

$$\mu_t(E) = \int_E \mathrm{d}\mu_t = \int_{S^{-t}E} \mathrm{d}\mu_0 = \mu_0(S^{-t}E) \tag{5}$$

where $S^{-t}E$ is the preimage of E an earlier time t. This equation simply means that the probability of $S^{-t}E$ at the initial time, is assumed to pertain to E at time t. With this definition, probability is conserved in phase space and in general[4] it flows like a compressible fluid. Taking much care, the evolution of the probability distributions may be used to define an evolution of the observables, introducing

$$\langle\phi\rangle_t = \int_{\mathcal{M}} \phi\,\mathrm{d}\mu_t \tag{6}$$

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[2] For instance, in simple cases one may take $\Gamma = (\mathbf{q}, \mathbf{p})$, and $I(\mathbf{q}, \mathbf{p}) = (\mathbf{q}, -\mathbf{p})$.

[3] Mathematically this condition is verified if the $\Gamma \in \mathcal{M}$ that yield different values for $\overline{\phi}(\Gamma)$ constitute a set of vanishing probability. This is a sufficient, not necessary, condition.

[4] In case of Hamiltonian dynamics, probabilities flow like incompressible fluids.

Under certain conditions, the mean values of the phase functions completely characterize the system, therefore one often refers to μ_t as to the *state* of the system at time t, which is to be distinguished from the microscopical phase $\Gamma \in \mathcal{M}$. A probability measure μ is called *invariant* if $\mu(E) = \mu(S^{-t}E)$ for all t and all measurable sets E.

At times μ_t has a density f_t, i.e. $\mathrm{d}\mu_t(\Gamma) = f_t(\Gamma)\mathrm{d}\Gamma$. In that case, the evolution of μ_t follows from the evolution of the normalized non-negative function f_t, determined by Eq. (5). Operating in Eq. (5) the change of coordinates $Y = S^tX$, i.e. $X = S^{-t}Y$, in the last integral of the following expression

$$\mu_t(E) = \int_E f_t(X)\mathrm{d}X = \int_{S^{-t}E} f_0(X)\mathrm{d}X \tag{7}$$

and:

$$\int_E f_t(X)\mathrm{d}X = \int_E f_0(Y)J^{-t}(Y)\mathrm{d}Y \tag{8}$$

where $J^{-t}(Y) = |(\partial S^{-t}X/\partial X)|_Y$ is the Jacobian of the transformation. As Eqs. (5)–(8) hold for all allowed subsets of $\mathcal{M}$, one can write

$$f_t(X) = f_0(S^{-t}X)J^{-t}(X) \tag{9}$$

For Hamiltonian dynamics, $J^{-t}(X) = 1$, hence $f_t(X) = f_0(S^{-t}X)$. In general, for the evolution of the observables one obtains:

$$\langle \phi \rangle_t = \int_{\mathcal{M}} \phi(\Gamma)f_t(\Gamma)\mathrm{d}\Gamma = \int_{\mathcal{M}} \phi(\Gamma)f_0(S^{-t}\Gamma)J^{-t}(\Gamma)\mathrm{d}\Gamma \tag{10}$$

Introducing $Y = S^{-t}\Gamma$ in the last integral, so that $\mathrm{d}\Gamma = J^t(Y)\mathrm{d}Y$, one finds:

$$\langle \phi \rangle_t = \int_{\mathcal{M}} \phi(S^tY)f_0(Y)J^{-t}(S^tY)J^t(Y)\mathrm{d}Y \tag{11}$$

Under suitable smoothness conditions for the dynamics and $\mathcal{M}$, probability is transported by the phase space points like the mass of a fluid, whose density f obeys the formal continuity equation:

$$\begin{aligned} \frac{\partial f}{\partial t} = -\nabla_\Gamma \cdot (Ff), \quad \frac{\mathrm{d}f}{\mathrm{d}t} = \frac{\partial f}{\partial t} + \nabla_\Gamma f \cdot F = -f\nabla_\Gamma \cdot F \\ = -f\Lambda \end{aligned} \tag{12}$$

Here $\Lambda = \nabla_\Gamma \cdot F$, called phase space expansion rate, is the divergence of the vector field F on $\mathcal{M}$, cf. Eq. (1). Introducing the total time derivative

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + F \cdot \nabla_\Gamma, \tag{13}$$

Eq. (12) may also be written as

$$\frac{\mathrm{d}}{\mathrm{d}t} \ln f = -\Lambda \tag{14}$$

Because the global existence and uniqueness of solutions of the equations of motion is practically assured for particle systems of physical interest,[5] one may safely assume that the solutions of the Liouville equation also exist and can be constructed by means of formal calculations. Various procedures are available for this purpose. For example, let us introduce the f-Liouvillean operator $\mathcal{L}$:

$$\mathcal{L} = -i(\nabla_\Gamma \cdot F + F \cdot \nabla_\Gamma), \quad \text{so that } \frac{\partial f}{\partial t} = -i\mathcal{L}f \tag{15}$$

and let us express $\partial f_t/\partial t$ to first order in the time increment Δt:

$$\frac{\partial f_t}{\partial t}(\Gamma) = -i(\mathcal{L}f_t)(\Gamma) = \frac{f_{t+\Delta t}(\Gamma) - f_t(\Gamma)}{\Delta t} + O(\Delta t) \tag{16}$$

It follows that

$$f_{\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t)f_0(\Gamma) + O(\Delta t^2) \tag{17}$$

$$\begin{aligned} f_{2\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t)f_{\Delta t}(\Gamma) + O(\Delta t^2) = \\ (1 - i\mathcal{L}\Delta t)^2 f_0(\Delta) + O(\Delta t^2) \end{aligned} \tag{18}$$

$$\vdots \tag{19}$$

$$f_{n\Delta t}(\Gamma) = (1 - i\mathcal{L}\Delta t)^n f_0(\Gamma) + nO(\Delta t^2) \tag{20}$$

Taking $\Delta t = t/n$, so that $\Delta \to 0$ and $nO(\Delta t^2) \to 0$ as $n \to \infty$, one obtains:

$$\begin{aligned} f_t(\Gamma) = \lim_{n\to\infty} \left(1 - \frac{it\mathcal{L}}{n}\right)^n f_0(\Gamma) = \sum_{n=0}^{\infty} \frac{(-it\mathcal{L})^n}{n!} f_0(\Gamma) \\ \equiv e^{-it\mathcal{L}} f_0(\Gamma) \end{aligned} \tag{21}$$

The question is now to connect Eq. (21) with Eq. (9). One can write

$$Y = S^tX = S^{t/n}\left(S^{t/n}\left(\cdots S^{t/n}(X)\cdots\right)\right) \tag{22}$$

Hence, the chain rule yields

$$\left.\frac{\partial Y}{\partial X}\right|_{X_i} = \left(\left.\frac{\partial S^{t/n}X}{\partial X}\right|_{X_{n-1}}\right)\left(\left.\frac{\partial S^{t/n}X}{\partial X}\right|_{X_{n-2}}\right)\cdots\left(\left.\frac{\partial S^{t/n}X}{\partial X}\right|_{X_0}\right) \tag{23}$$

where $X_j = S^{jt/n}X_0$, and X_0 is the initial point of a trajectory. One can expand to first order each derivative in brackets as follows:

$$\left.\frac{\partial\left(S^{t/n}X\right)}{\partial X}\right|_{X_j} = \frac{\partial}{\partial X}\left(X + F\Delta t + O(\Delta t^2)\right)\Big|_{X_j} \tag{24}$$

and further

$$\left.\frac{\partial\left(S^{t/n}X\right)}{\partial X}\right|_{X_j} = 1 + \left.\frac{\partial F}{\partial X}\right|_{X_j}\Delta t + O(\Delta t^2) = e^{\left.\frac{\partial F}{\partial X}\right|_{X_j}\Delta t} + O(\Delta t^2) \tag{25}$$

1 being the identity matrix. Substituting Eq. (25) in Eq. (23), and noting that the exponential operators do not commute in general, the $n \to \infty$ limit leads to a so-called *left ordered* exponential, which can also be expressed as a Dyson series:

$$\begin{aligned} e_L^{\int_0^t T(S^sX)\mathrm{d}s} = 1 + \int_0^t \mathrm{d}t_1 T(S^{t_1}X) + \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 T(S^{t_1}X)T(S^{t_2}X) \\ + \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 T(S^{t_1}X)T(S^{t_2}X)T(S^{t_3}X) + \cdots \end{aligned}$$

where the time dependent matrix

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[5] Global solution means that particles do no cease to exist after a while; Uniqueness implies that the same particles do not exist at once along distinct trajectories. If these properties are violated, the model under investigation must be discarded.

$$T(S^sX) = \left.\frac{\partial F}{\partial X}\right|_{S^sX} \tag{26}$$

is the Jacobian matrix of F computed at the point S^sX. Considering that the identity $\det(e^L) = \exp(\mathrm{Tr}L)$ holds for left ordered exponentials as well, one obtains:

$$\det\left(e_L^{\int_0^t T(S^sX)\mathrm{d}s}\right) = \exp\left\{\int_0^t \nabla_\Gamma \cdot F\left(S^sX\right)\mathrm{d}s\right\} = \int_0^t \Lambda\left(S^sX\right)\mathrm{d}s \tag{27}$$

Which implies that:

$$J^t(X) = e^{\int_0^t \Lambda(S^uX)\mathrm{d}u} = e^{\int_{-t}^0 \Lambda(S^{t+s}X)\mathrm{d}s} = \frac{1}{J^{-t}\left(S^tX\right)} = \frac{1}{J^{-t}(Y)} \tag{28}$$

where we have taken $u = t + s$ in the second integral. Eq. (28) is obvious for compressible fluids: a fluid element about X varies in a time t by a factor which is the inverse of the variation of the fluid element about Y, when tracing backwards its trajectory. Consequently $J^{-t}(S^tX)J^t(X) = 1$, and Eq. (9) may be rewritten as:

$$f_t(X) = f_0(S^{-t}X)e^{-\int_{-t}^0 \Lambda(S^sX)\mathrm{d}s} \tag{29}$$

while Eq. (11) takes the interesting form

$$\langle\phi\rangle_t = \int_{\mathcal{M}} \left(\phi \circ S^t\right)(X) f_0(X)\mathrm{d}X = \langle\phi \circ S^t\rangle_0 \tag{30}$$

2.1. Ergodicity and mixing

Let μ be one invariant probability distribution and ϕ an integrable phase function. The following statements are equivalent:

E1. $\overline{\phi}(\Gamma) = \langle\phi\rangle_\mu$, except for a set of vanishing μ probability;

E2. except for a set of vanishing μ probability, $\tau_E(\Gamma) = \mu(E)$, where $E \subset \mathcal{M}$ is a μ-measurable set and

$$\tau_E(\Gamma) = \lim_{t\to\infty}\frac{1}{t}\int_0^t \chi_E(S^s\Gamma)\mathrm{d}s; \text{ with } \chi_E(\Gamma) = \begin{cases} 1 & \text{if } \Gamma \in E \\ 0 & \text{else} \end{cases} \tag{31}$$

is the mean time in E;

E3. let ϕ be μ-integrable and let ϕ be a constant of motion (i.e.$\phi(S^t\Gamma) = \phi(\Gamma)$ for all t and all Γ). Then $\phi(\Gamma) = C$ μ-almost everywhere, for a given $C \in \mathbb{R}$;

E4. the dynamical system $(S, \mathcal{M}, \mu)$ is *metrically indecomposable*, i.e. given the invariant set E (which means $S^{-t}E = E$), either $\mu(E) = 0$ or $\mu(E) = 1$.

We call *ergodic* the dynamical systems that verify these statements. This is a very strong property because ϕ can be any integrable function. Physics concerns, instead, only a few phase variables that are physically relevant.

The following statements are equivalent too:

M1. For every pair of measurable sets $D, E \subset \mathcal{M}$ one has:

$$\lim_{t\to\infty}\mu(S^{-t}D \cap E) = \mu(D)\mu(E) \tag{32}$$

M2. for all $\phi, \psi \in L_2(\mathcal{M}, \mu)$ the following holds:

$$\lim_{t\to\infty}\langle(\phi \circ S^t)\psi\rangle_\mu = \langle\phi\rangle_\mu\langle\psi\rangle_\mu \tag{33}$$

We call *mixing* the dynamical systems that verify these two statements. Mixing is an even stronger property than ergodicity, in the sense that mixing systems are also ergodic, whereas not all ergodic systems are mixing.

For dynamics, which are mixing with respect to a probability measure with density h, $d\mu = hd\Gamma$ say, one can prove that an initial state characterized by a probability density f_0 eventually converges to the state of density h. To prove that, consider the phase functions ϕ and ψ, for which one can write:

$$\lim_{t\to\infty}\langle(\phi \circ S^t) \cdot \psi\rangle_h = \lim_{t\to\infty}\langle\phi \circ S^t\rangle_h\langle\psi\rangle_h = \langle\psi\rangle_h \int d\Gamma\phi(S^t\Gamma)h(\Gamma) = \langle\psi\rangle_h \int d\Gamma\phi(\Gamma)S^{*t}h(\Gamma) = \langle\psi\rangle_h\langle\phi\rangle_h$$

where the superscript * denotes the distribution function propagator for a period time t. Then, for a time dependent probability distribution f_t which vanishes at least where h does, let us introduce $R_t = f_t/h$:

$$\int R_t(\Gamma)h(\Gamma)d\Gamma = \int f_t(\Gamma)d\Gamma = 1; \quad \int \frac{1}{R_t(\Gamma)}f_t(\Gamma)d\Gamma = \int h(\Gamma)d\Gamma = 1 \tag{34}$$

for all times t, and we obtain:

$$\langle\phi\rangle_t = \int \phi(\Gamma)f_t(\Gamma)d\Gamma = \int \phi(\Gamma)R_t(\Gamma)h(\Gamma)d\Gamma = \langle\phi \cdot R_t\rangle_h \tag{35}$$

We can also write, by definition:

$$\langle\phi\rangle_t = \int \phi(\Gamma)f_t(\Gamma)d\Gamma = \int \phi(S^t\Gamma)f_0(\Gamma)d\Gamma = \int \phi(S^t\Gamma)R_0(\Gamma)h(\Gamma)d\Gamma \tag{36}$$

from which, the mixing condition produces the convergence to the steady state of density h:

$$\lim_{t\to\infty}\langle\phi\rangle_t = \int \phi(S^t\Gamma)R_0(\Gamma)h(\Gamma)d\Gamma = \langle(\phi \circ S^t)R_0\rangle_h \to \langle\phi\rangle_h\langle R_0\rangle_h = \langle\phi\rangle_h \tag{37}$$

In other words, probability densities for finite systems, if they are both stationary and mixing, are attractors in the space of probability densities.

However, this proof of convergence to a mixing stationary state is deceitfully simple. Although it is a very strong property, in general mixing does not suffice to prove convergence to a steady state, because it amounts to the decay in time of the microscopic correlations within already stationary macroscopic states and not to the decorrelation of the initial state from the final state.

3. Linear response

Let us address the response of a given system to external actions. As an example, consider a system of N particles in contact with a thermal bath at inverse temperature β, described by the following Hamiltonian:

$$H(\Gamma) = H_0(\Gamma) + \lambda A(\Gamma) \tag{38}$$

where λ is a small parameter and A perturbs the canonical equilibrium:

$$f_0 = \exp(-\beta H_0) \Big/ \int \mathrm{d}\Gamma \exp(-\beta H_0) \tag{39}$$

After some time, a new canonical equilibrium is established which, to the first order in λ, is given by:

$$\begin{aligned} f &= \frac{e^{-\beta H_0} e^{-\beta\lambda A}}{\int \mathrm{d}\Gamma e^{-\beta H_0} e^{-\beta\lambda A}} \\ &= \frac{e^{-\beta H_0}\left[1 - \beta\lambda A + O(\beta^2\lambda^2 A^2)\right]}{\int \mathrm{d}\Gamma e^{-\beta H_0}\left[1 - \beta\lambda A + O(\beta^2\lambda^2 A^2)\right]} \simeq f_0 \frac{1 - \lambda\beta A}{1 - \lambda\beta\langle A\rangle_0} \\ &\simeq f_0(\Gamma)[1 - \lambda\beta(A(\Gamma) - \langle A\rangle_0)] \end{aligned} \tag{40}$$

where, $\langle\cdot\rangle_0$ denotes averaging with respect to f_0. The effect of the perturbation on a given observable ϕ, is then expressed by:

$$\begin{aligned} \langle\phi\rangle_\lambda - \langle\phi\rangle_0 &= \int \mathrm{d}\Gamma \phi(\Gamma)[f(\Gamma) - f_0(\Gamma)] \\ &\simeq -\lambda\beta[\langle\phi A\rangle_0 - \langle\phi\rangle_0\langle A\rangle_0] \end{aligned} \tag{41}$$

which is the correlation of the observable ϕ with the perturbation A, with respect to the state expressed by f_0. Taking $\phi = A = H_0$, one obtains an expression for the heat capacity at constant volume C_V, which expresses the response of the system to temperature variations. Indeed, defining C_V as

$$C_V = \frac{\partial\langle H_0\rangle_0}{\partial T} = \frac{\mathrm{d}\beta}{\mathrm{d}T}\frac{\partial\langle H_0\rangle_0}{\partial\beta} = \frac{\langle H_0^2\rangle_0 - \langle H_0\rangle_0^2}{k_B T^2} \tag{42}$$

Eqs. (41) and (42) yield:

$$\begin{aligned} \left.\frac{\partial\langle H_0\rangle}{\partial\lambda}\right|_{\lambda=0} &= \lim_{\lambda\to 0}\frac{\langle H_0\rangle_\lambda - \langle H_0\rangle_0}{\lambda} = -\beta\left[\langle H_0^2\rangle_0 - \langle H_0\rangle_0^2\right] \\ &= -k_B T^2 C_V \end{aligned} \tag{43}$$

More in general, consider time dependent perturbations of form $-\mathcal{F}(t)A(\Gamma)$:

$$H(\Gamma, t) = H_0(\Gamma) - \mathcal{F}(t)A(\Gamma) \tag{44}$$

and split the corresponding evolution operator in two parts:s

$$i\mathcal{L}_0 f = \{f, H_0\}, \quad i\mathcal{L}_{\text{ext}}(t)f = -\mathcal{F}(t)\{f, A\} \tag{45}$$

where $\{\cdot\}$ are the Poisson brackets. One has $i\mathcal{L}_0 f_0 = 0$, which means that f_0 is invariant for the unperturbed dynamics. Then, the solution of the Liouville equation

$$\frac{\partial f}{\partial t} = -i(\mathcal{L}_0 + \mathcal{L}_{\text{ext}}(t))f \tag{46}$$

can be expressed by:

$$\begin{aligned} f_t(\Gamma) &= e^{it\mathcal{L}_0} f_0(\Gamma) - i\int_0^t \mathrm{d}t' e^{-i(t-t')\mathcal{L}_0}\mathcal{L}_{\text{ext}}(t') f_{t'}(\Gamma) \\ &= f_0(\Gamma) - i\int_0^t \mathrm{d}t' e^{-i(t-t')\mathcal{L}_0}\mathcal{L}_{\text{ext}}(t') f_0(\Gamma) \\ &\quad + \text{higher order in } \mathcal{L}_{\text{ext}} \end{aligned}$$

as proved by inspection. If the deviations from the unperturbed system are considered small, the higher orders in $\mathcal{L}_{\text{ext}}$ can be omitted. Then Eq. (41) implies:

$$\langle\phi\rangle_t - \langle\phi\rangle_0 \simeq \int \mathrm{d}\Gamma\phi(\Gamma)\int_0^t \mathrm{d}t' e^{-i(t-t')\mathcal{L}_0}\mathcal{F}(t')\{f_0, A\} \tag{47}$$

where

$$\{f_0, A\} = \{H_0, A\}\frac{\partial f_0}{\partial H_0} = \beta f_0 \frac{\mathrm{d}A}{\mathrm{d}t} \tag{48}$$

Eventually, one obtains:

$$\langle\phi\rangle_t - \langle\phi\rangle_0 \simeq \int_0^t \mathrm{d}t' R(t - t')\mathcal{F}(t') \tag{49}$$

where $R(t)$ is the response function:

$$R(t) = \beta\langle\dot{A}(\phi\circ S^t)\rangle_0 = \beta\int \mathrm{d}\Gamma f_0(\Gamma)\frac{\mathrm{d}A}{\mathrm{d}t}(\Gamma)e^{it\mathcal{F}_0}\phi(\Gamma) \tag{50}$$

Once again, the macroscopic nonequilibrium behaviour of a given system has been related solely to the correlations of microscopic fluctuating quantities, computed with respect to the relevant equilibrium ensemble. An analogous result comes when considering the frequency dependent formulation of linear response, cf. e.g. [4], which finds relevant implications in optics and acoustics.

Eq. (49) suggests that even the linear response is in general affected by memory effects, hence the Markovian behaviour appears to be either very special or only approximately valid. This implies, for instance, that all nonequilibrium fluids have a viscoelastic behaviour. In practice, however, in normal fluids this behaviour arises only exceedingly far from equilibrium.

Recently, it has been shown that this approach applies to the case of perturbation of non equilibrium steady states, if they are represented by a regular probability density, as in the presence of noise, cf. Refs. [5,6].

Differently, the invariant phase space probability distribution μ of a dissipative system is singular and supported on a fractal attractor. Consequently, it is not obvious anymore that the statistical features induced by a perturbation can be related to the unperturbed statistics. The reason is that even very small perturbations may lead to microscopic phase whose probability vanishes in the unperturbed state. In such a case, the information contained in μ is irrelevant.

Indeed, Ruelle [7] showed that in certain cases[6] a perturbation $\delta\Gamma$ about a microstate Γ and its evolution $S^t\delta\Gamma$ can be decomposed in two parts, $(S^t\delta\Gamma)_\parallel$ and $(S^t\delta\Gamma)_\perp$, respectively perpendicular and parallel to the fibres of the attractor:

$$S^t\delta\Gamma = (S^t\delta\Gamma)_\parallel + (S^t\delta\Gamma)_\perp$$

The first addend can be related to the dynamics on the attractor, while the second may not.

Later, it has been pointed out [8] that this difficulty should not concern systems of many interacting particles. In those cases, rather than the full phase space, one considers the much lower dimensional projections concerning

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[6] Concerning certain smooth, uniformly hyperbolic dynamical systems.

the few physically relevant observables, i.e. the marginals of singular phase space measures, on spaces of sufficiently lower dimension, which are usually regular [9,10]. These facts can be briefly recalled as follows. Ruelle showed that the effect of a perturbation $\delta F(t) = \delta F_\parallel(t) + \delta F_\perp(t)$ on the response of a generic (smooth enough) observable ϕ is given by:

$$\langle\phi\rangle_t - \langle\phi\rangle_0 = \int_0^t R_\parallel^{(\phi)}(t-\tau)\delta F_\parallel(\tau)d\tau + \int_0^t R_\perp^{(\phi)}(t-\tau)\delta F_\perp(\tau)d\tau \qquad (51)$$

where the subscript 0 denotes averaging with respect to μ, $R_\parallel^{(\phi)}$ may be expressed in terms of correlation functions evaluated with respect to μ, while $R_\perp^{(\phi)}$ depends on the dynamics along the stable manifold, hence it may not.

Let us adopt the point of view of Ref. [8]. For a d-dimensional dissipative dynamical system consider, for simplicity, an impulsive perturbation $\Gamma \to \Gamma + \delta\Gamma$, such that all components of $\delta\Gamma$ vanish except one, denoted by $\delta\Gamma_i$. The probability distribution μ is correspondingly shifted by $\delta\Gamma$, and turns into a non-invariant distribution μ_0, whose evolution μ_t tends to μ in the $t \to \infty$ limit. For every measurable set $E \subset \mathcal{M}, \mu_0(E)$ equals $\mu(E - \delta\Gamma)$,[7] and $\mu_t(E)$ is computed as explained in Section 2. Taking $\phi(\Gamma) = \Gamma_i$, one obtains:

$$\langle\Gamma_i\rangle_t - \langle\Gamma_i\rangle_0 = \int \Gamma_i \mathrm{d}\mu_t(\Gamma) - \int \Gamma_i \mathrm{d}\mu(\Gamma) \qquad (52)$$

Let us now approximate the singular μ, coarse graining $\mathcal{M}$ with an ϵ-partition made of a finite set of d-dimensional hypercubes $\Lambda_k(\epsilon)$ of side ϵ and centers Γ_k. The corresponding approximations of μ and of μ_t are given by the probabilities $P_k(\epsilon)$ and $P_{t,k}(\epsilon;\delta\Gamma)$ of the hypercubes $\Lambda_k(\epsilon)$, where:

$$P_k(\epsilon) = \int_{\Lambda_k(\epsilon)} \mathrm{d}\mu(\Gamma), \quad P_{t,k}(\epsilon) = \int_{\Lambda_k(\epsilon)} \mathrm{d}\mu_t(\Gamma). \qquad (53)$$

The coarse grained invariant density $\rho(\Gamma;\epsilon)$ is given by:

$$\rho(\Gamma;\epsilon) = \sum_k \rho_k(\Gamma;\epsilon), \quad \text{with} \quad \rho_k(\Gamma;\epsilon) = \begin{cases} P_k(\epsilon)/\epsilon^d & \text{if } x \in \Lambda_k(\epsilon) \\ 0 & \text{else} \end{cases} \qquad (54)$$

If Z_i is the number of one-dimensional bins of form $\left[\Gamma_i^{(q)} - \epsilon/2, \Gamma_i^{(q)} + \epsilon/2\right), q \in \{1, 2, \ldots, Z_i\}$, in the i-th direction, marginalizing the approximate distribution yields the quantities:

$$p_i^{(q)}(\epsilon) = \int_{\Gamma_i^{(q)} - \frac{\epsilon}{2}}^{\Gamma_i^{(q)} + \frac{\epsilon}{2}} \left\{ \int \rho(\Gamma;\epsilon) \prod_{j \neq i} \mathrm{d}\Gamma_j \right\} \mathrm{d}\Gamma_i, \qquad (55)$$

each of which is the invariant probability that the coordinate Γ_i of Γ lie in one of the Z_i bins. Similarly, one gets the marginal of the evolving approximate probability:

$$p_{i,t}^{(q)}(\epsilon) = \int_{\Gamma_i^{(q)} - \frac{\epsilon}{2}}^{\Gamma_i^{(q)} + \frac{\epsilon}{2}} \left\{ \int \rho_t(\Gamma;\epsilon) \prod_{j \neq i} \mathrm{d}\Gamma_j \right\} \mathrm{d}\Gamma_i, \qquad (56)$$

Dividing by ϵ, one obtains the coarse grained marginal probability densities $\rho_i^{(q)}(\epsilon)$ and $\rho_{t,i}^{(q)}(\epsilon)$, as well as the ϵ-approximate response function:

$$B_i^{(q)}(\Gamma_i, \delta\Gamma, t, \epsilon) = \frac{1}{\epsilon}\left[p_{t,i}^{(q)}(\epsilon) - p_i^{(q)}(\epsilon)\right] = \rho_{t,i}^{(q)}(\epsilon) - \rho_i^{(q)}(\epsilon) \qquad (57)$$

Ref. [8] shows that the right hand side of Eq. (57) tends to a regular function of Γ_i under the $Z_i \to \infty, \epsilon \to 0$ limits. Consequently, $B_i^{(q)}(\Gamma_i, \delta\Gamma, t, \epsilon)$ yields an expression similar to that of standard response theory, in the sense that it depends solely on the unperturbed state, although that is supported on a fractal set. There are exceptions to this conclusion, most notably those discussed by Ruelle. But for most systems of physical interest, such as systems of many interacting particles, this is the expected result. The idea is that the projection procedure makes unnecessary the explicit calculation of $R_\perp^{(\phi)}$ in Eq. (51), although $R_\perp^{(\phi)}$ does not need to be negligible [11]. Therefore, apart from peculiar situations, the response may be referred only to the unperturbed dynamics, as in the standard theory.

4. Onsager–Machlup: response from small deviations

The classical theory of fluctuations, developed by Onsager and Machlup [12,13] to quantify the probability of temporal fluctuations paths, is based on the following assumptions:

- **A1.** Onsager regression hypothesis: the decay of a system from a nonequilibrium state produced by a spontaneous fluctuation, obeys on average the macroscopic law describing the decay from the same state produced by a macroscopic constraint that has been suddenly removed;
- **A2.** the observables are Gaussian random variables (i.e. the probability density of m values taken at m consecutive instants of time is an m-dimensional Gaussian);
- **A3.** the probability density $P(\Gamma)$ of the microstate Γ obeys Boltzmann's principle:

  $$k_B \log P(\Gamma) = \mathcal{S}(\Gamma) + \text{const} \qquad (58)$$
- **A4.** the state $S^t\Gamma$ is statistically independent of the state $S^{t'}\Gamma$ for $|t - t'| > \tau_d, \tau_d$ being the decorrelation time;
- **A5.** the microscopic dynamics is time reversal invariant;
- **A6.** the vector of observables $\alpha = (\alpha_1, \ldots, \alpha_n)$ is chosen so that its evolution is Markovian. This is possible if n is neither too small nor too large in such a way that:
  - α_i represents a macroscopic quantity referring to a subsystem containing very many particles;
  - α_i is an algebraic sum of molecular variables, so that by the Central Limit Theorem its fluctuations are Gaussians centered on its average (equilibrium) value;
  - α_i must be an even function of the molecular variables that are odd under time reversal (microscopic time reversal invariance);
- **A7.** the system is in local thermodynamic equilibrium;
- **A8.** the fluxes $\dot{\alpha}_i$ depend linearly on the thermodynamic forces X_i:

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[7] The set $E - \delta\Gamma$ is defined by $\{\Gamma \in \mathcal{M} : \Gamma + \delta\Gamma \in E\}$.

$$\dot{\alpha}_i = \sum_{j=1}^{n} L_{ij} X_j, \quad X_i = \sum_{j=1}^{n} R_{ij}\dot{\alpha}_j; \tag{59}$$

A9. the process is stationary: i.e. given the times $t_1, t_2, \ldots, t_p$ and the n-dimensional vectors $\alpha^{(1)}, \alpha^{(2)}, \ldots, \alpha^{(p)}$, the probabilities $F_{i,p}, i = 1, \ldots, n$, that each component of the observable vector is smaller by value than the corresponding component of the vector sequence $\alpha^{(k)}$ at the corresponding times t_k satisfy:

$$F_{i,p}\left(\alpha_i \leqslant \alpha_i^{(k)}, t_k, k = 1, \ldots, p\right) = F_{i,p}\left(\alpha_i \leqslant \alpha_i^{(k)}, t_k + \tau, k = 1, \ldots, p\right) \tag{60}$$

for all τ and, analogously, the corresponding probability densities $f_{i,p}$, satisfy

$$f_{i,p}\left(\alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p\right) = f_{i,p}\left(\alpha_i = \alpha_i^{(k)}, t_k + \tau, k = 1, \ldots, p\right) \tag{61}$$

where

$$F_{i,p}\left(\alpha_i \leqslant \alpha_i^{(k)}, t_k, k = 1, \ldots, p\right) = \int_{-\infty}^{\alpha_i^{(1)}} d\alpha_i^{(1)} \cdots \int_{-\infty}^{\alpha_i^{(p)}} d\alpha_i^{(p)} f_{i,p}\left(\alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p\right)$$

We thus emphasize that, unless the hypotheses listed above are fulfilled, the use of the classical response theory traced by Onsager and Machlup may be misleading, in particular when dealing with systems pulled out of equilibrium. For simplicity, let α be the vector of the deviations from the equilibrium values. Then, the entropy $\mathcal{S}$ is a function of the observables α, which can be expanded about its equilibrium value $\mathcal{S}_0$ as:

$$\mathcal{S} = \mathcal{S}_0 - \frac{1}{2}\sum_{i,j=1}^{n} s_{ij}\alpha_i\alpha_j + \text{higher order in } \alpha \tag{62}$$

There is no linear term in α because $\mathcal{S}_0$ is the maximum of $\mathcal{S}$. Correspondingly, the thermodynamic forces are expressed by

$$X_i = \frac{\partial \mathcal{S}}{\partial \alpha_i} = -\sum_{j=1}^{n} s_{ij}\alpha_j, \quad i = 1, \ldots, n \tag{63}$$

which implies

$$\sum_{j=1}^{n} \left[R_{ij}\dot{\alpha}_j + s_{ij}\alpha_j\right] = 0, \quad i = 1, \ldots, n \tag{64}$$

To compute the evolution of α, let us introduce the functions

$$\Phi\left(\dot{\alpha}, \dot{\beta}\right) = \frac{1}{2}\sum_{i,j=1}^{n} R_{ij}\dot{\alpha}_i\dot{\beta}_j, \quad \Psi(X, Y) = \frac{1}{2}\sum_{i,j=1}^{n} L_{ij}X_iX_j \tag{65}$$

Which characterize the real evolution only when $\dot{\alpha} = \dot{\beta}$ are the real evolving fluxes and when $X = Y$ are the real thermodynamic forces, in which cases we have:

$$\dot{\mathcal{S}} = 2\Phi(\dot{\alpha}, \dot{\alpha}) = 2\Psi(X, X) \tag{66}$$

The molecular chaos may be accounted for by a random perturbation, which turns Eq. (64) into

$$\sum_{j=1}^{n} \left[R_{ij}\dot{\alpha}_j + s_{ij}\alpha_j\right] = \epsilon_i, \quad \langle \epsilon_i \rangle = 0, \quad i = 1, \ldots, n \tag{67}$$

where ϵ_i is a random force which allows different paths with different probabilities and which does no net work.

Let $f_{i,1}\left(\alpha_i^{(1)}, t_1\right)$ be the probability density for the ith observable to take values close to $\alpha_i^{(1)}$ at time t_1. By assumption **A3**, $f_{i,1}$ is independent of t_1. Let $f_{i,1}\left(\alpha_i^{(k)}, t_k | \alpha_{i-1}^{(k-1)}, t_{k-1}\right)$ be the conditional probability density for the ith observable to take values close to $\alpha_i^{(k)}$ at time t_k, given that it was $\alpha_{i-1}^{(k-1)}$ at time t_{k-1}. Because of the Markov property and of **A3**, one has:

$$f_{i,p}\left(\alpha_i = \alpha_i^{(k)}, t_k, k = 1, \ldots, p\right) \tag{68}$$

$$= f_{i,1}\left(\alpha_i^{(p)}, t_p | \alpha_{i-1}^{(p-1)}, t_{p-1}\right) \cdots f_{i,1}\left(\alpha_i^{(2)}, t_2 | \alpha_i^{(1)}, t_1\right) f_{i,1}\left(\alpha_i^{(1)}, t_1\right) \tag{69}$$

$$= f_{i,1}\left(\alpha_i^{(p)}, t_p | \alpha_{i-1}^{(p-1)}, t_{p-1}\right) \cdots f_{i,1}\left(\alpha_i^{(2)}, t_2 | \alpha_i^{(1)}, t_1\right) e^{\mathcal{S}(\alpha^{(1)})/k_B} \tag{70}$$

with two constraints

$$\text{(a)} \lim_{\tau \to 0} f_{i,1}\left(\alpha_i, t_1 + \tau | \alpha_i^{(1)}, t_1\right) = K\delta\left(\alpha - \alpha^{(1)}\right) \tag{71}$$

due to the fact that $\tau \to 0$ is the limit in which α deterministically approaches $\alpha^{(1)}$, and

$$\text{(b)} \lim_{\tau \to \infty} f_{i,1}\left(\alpha_i, t_1 + \tau | \alpha_i^{(1)}, t_1\right) = e^{\mathcal{S}(\alpha^{(1)})/k_B} \tag{72}$$

representing the loss of correlations between the time t_1 and the time $t_1 + \tau$. Solving the Langevin equation (67), $f_{i,1}\left(\alpha_i, t_1 + \tau | \alpha_1^{(1)}, t_1\right)$ can be explicitly given. Let us now turn to the case with $n = 1$:

$$R\dot{\alpha} + s\alpha = \epsilon \tag{73}$$

this process is described by:

$$f_1\left(\alpha, t + u | \alpha^{(0)}, t\right) = \frac{s \exp\left\{-\frac{s\left(\alpha - \alpha^{(0)}e^{-su/R}\right)^2}{2k_B\left(1 - e^{-2su/R}\right)}\right\}}{\sqrt{2\pi k_B}\sqrt{1 - e^{-2su/R}}} \tag{74}$$

With this information and with Ito's discretization convention [12], one eventually obtains:

$$f_1\left(\alpha, t + \tau | \alpha^{(0)}, t\right) = \left(\frac{1}{2k_B}\right)^p \left(\frac{sR}{\pi\delta\tau}\right)^{p/2} \times \tag{75}$$

$$\int d\alpha^{(1)} \cdots \int d\alpha^{(p)} \exp\left\{-\frac{R}{4k_B}\sum_{k=1}^{p}\left[\dot{\alpha}^{(k)} + \frac{s}{R}\alpha^{(k+1)}\right]^2 \delta\tau\right\} \tag{76}$$

Under the $p \to \infty, \delta\tau \to 0$ limits, with $\tau = p\delta\tau$, the sum in the exponential tends to the integral along the path:

$$\int_t^{t+\tau} \left[\dot{\alpha}(t') + \frac{s}{R}\alpha(t')\right]^2 dt' \tag{77}$$

which must be minimized to maximize the probability. Analogously, the n-dimensional case requires the minimization of:

$$\int_t^{t+\tau} \sum_{i=1}^{n} \left[\dot{\alpha}_i(t') + \frac{s_i}{R_i}\alpha_i(t')\right]^2 dt'. \tag{78}$$

Here, the integrand can be expressed as

$$\mathcal{L}(\alpha,\dot\alpha) = 2\Phi(\dot\alpha,\dot\alpha) - 2\dot S(\alpha) + 2\Psi(X(\alpha),X(\alpha)) \tag{79}$$

and the path of minimum integral follows from the Lagrange equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial\mathcal{L}}{\partial\dot\alpha} - \frac{\partial\mathcal{L}}{\partial\alpha} = 0, \quad \text{which yields } R_j\ddot\alpha_j - \frac{s_j^2}{R_j}\alpha_j = 0, \quad j = 1,\ldots,n \tag{80}$$

These second order differential equations are equivalent to pairs of first order equations. Indeed, their general solution

$$\alpha_j(t) = C_{j1}e^{-s_jt/R_j} + C_{j2}e^{s_jt/R_j} \tag{81}$$

requires $C_{j2} = 0$ when the $t \to \infty$ limit is considered–in which case we have relaxation to equilibrium from a non-equilibrium initial condition–while it requires $C_{j1} = 0$ when the previous history, beginning with an equilibrium state at $t = -\infty$, is considered. The first case is solution of the differential equation

$$\dot\alpha_j + \frac{s_j}{R_j}\alpha_j = 0 \tag{82}$$

and the second case corresponds to

$$\dot\alpha_j - \frac{s_j}{R_j}\alpha_j = 0. \tag{83}$$

We thus have two evolutions, which are symmetric under time reversal: one describes the relaxation to equilibrium, in accord with hydrodynamics; the other treats fluctuations away from equilibrium, and is the first example of the so-called *adjoint hydrodynamics* [14]. In the large n limit, the most probable path becomes the only path of positive probability and a justification of hydrodynamics is obtained, starting from a mesoscopic description.

These results are crucially based on the Gaussian distributions, hence they are restricted to small deviations, from which the linear response about equilibrium states is derived.

Considering large deviations, this theory has been generalized to fluctuations about nonequilibrium steady states, which are not symmetric under time reversal [14]. For dissipative deterministic particle systems, that are time reversal invariant, it has been shown that similar asymmetries may arise, when particles interact [15].

5. Fluctuation Relations: response from large deviations

In 1993, the paper [16] addressed the question of the fluctuations of the entropy production rate in a pioneering attempt towards a unified theory of a wide range of non-equilibrium phenomena. In particular, a *Fluctuation Relation* (FR) was there derived and tested. Obtained on purely dynamical grounds, it constitutes one of the few general exact results for systems almost arbitrarily far from equilibrium, while close to equilibrium it is consistent with the Green–Kubo and Onsager relations. This FR reads:

$$\frac{\mathrm{Prob}_\tau(\sigma \approx A)}{\mathrm{Prob}_\tau(\sigma \approx -A)} = e^{\tau A} \tag{84}$$

where A and $-A$ are average values of the normalized power dissipated in a long time τ in a driven system, denoted by σ and $\mathrm{Prob}_\tau(\sigma \approx \pm A)$ is the steady state probability of observing values close to $\pm A$.

This relation constitutes a *large deviation* result: for large τ, any $A \neq \langle\sigma\rangle$ lies many standard deviations away from the mean. In other words, A corresponds to a large (macroscopic) deviation from the macroscopically observable value $\langle\sigma\rangle$.

The FR (84) was derived for the following *isoenergetic* model of a 2-dimensional shearing fluid:

$$\begin{cases} \frac{d}{dt}\mathbf{q}_i = \frac{\mathbf{p}_i}{m} + \gamma y_i\hat{\mathbf{x}} \\ \frac{d}{dt}\mathbf{p}_i = \mathbf{F}_i(\mathbf{q}) + \gamma p_i^{(y)}\hat{\mathbf{x}} - \alpha_{th}\mathbf{p}_i \end{cases} \tag{85}$$

where γ is the shear rate in the y direction, $\hat{\mathbf{x}}$ is the unit vector in the x-direction, and the friction term α_{th}, called “thermostat”, takes the form

$$\alpha_{th}(\Gamma) = -\frac{\gamma}{\sum_{i=1}^{N}\mathbf{p}_i^2}\sum_{i=1}^{N}p_i^{(x)}p_i^{(y)} \tag{86}$$

as prescribed by Gauss’ principle of least constraint, in order to keep the internal energy fixed.

This molecular dynamics model was chosen by the authors of [16] because its phase space expansion rate Λ is proportional to α_{th}. Hence a dynamical quantity, could be related to the energy dissipation rate divided by $\sum\mathbf{p}_i^2$. The FR is parameter-free and, being dynamical in nature, it applies almost arbitrarily far from equilibrium as well as to small systems.

Gallavotti and Cohen clearly identified the mathematical framework within which Ref. [16] had been developed, introducing the following [17–20]:

Chaotic Hypothesis: A reversible many-particle system in a stationary state can be regarded as a transitive Anosov system for the purpose of computing its macroscopic properties.

Anosov systems can indeed be proven to have probability distributions of the kind assumed in [16]. The result is a steady state FR for the fluctuations of Λ, which we call Λ-FR and which will be described below. As the Anosov property practically means a high degree of randomness, analogous results have been obtained first for finite state space Markov chains and later for many other stochastic processes [21–23]. Stochastic processes are easier to handle than deterministic dynamics, but ambiguities affect their observables, except for special cases. The reader is addressed to the numerous existing review papers, such as Refs. [24,5,25]. We focus now on some specific results for deterministic dynamics.

5.1. The Gallavotti–Cohen approach

The idea proposed by Gallavotti and Cohen is that dissipative, reversible, transitive Anosov maps, $S : \mathcal{M} \to \mathcal{M}$, are idealizations of nonequilibrium particle systems [18]. That the system evolves with discrete or continuous time was thought to be a side issue [18]. The Λ-FR for Anosov maps relies on time reversibility and on the fact that these dynamical systems admit arbitrarily fine *Markov* partitions [26]. These are subdivisions of $\mathcal{M}$ in cells with disjoint interiors and with boundaries forming invariant sets, which in two dimensions consist of pieces of stable and unstable manifolds. Gallavotti and Cohen further assumed that the dynamics is transitive, i.e. that a typical trajectory explores all regions of $\mathcal{M}$, as finely as one wishes. This structure justifies the probability (Lyapunov) weights of Eq. (1) in Ref. [16], from which the Λ-FR emerges.

Let the dynamics be given by $X_{k+1} = SX_k$ and introduce the phase space expansion rate $\Lambda(X) = \log J(X)$, where J is the Jacobian determinant of S. The dynamics is called *dissipative* if $\langle\Lambda\rangle < 0$, where $\langle . \rangle$ is the steady state phase space average. Then, consider the dimensionless phase space contraction rate e_τ, obtained along a trajectory segment $w_{X,\tau}$ with origin at $X \in \mathcal{M}$ and duration τ, defined by:

$$e_\tau(X) = \frac{1}{\tau\langle\Lambda\rangle}\sum_{k=-\tau/2}^{\tau/2-1}\Lambda(S^kX) \tag{87}$$

Let J^u be the Jacobian determinant of S restricted to the unstable manifold V^+, i.e. the product of the asymptotic separation factors of nearby points, along the directions in which distances asymptotically grow at an exponential rate. *If the system is Anosov*, the probability that $e_\tau(X) \in B_{p,\epsilon} \equiv (p-\epsilon, p+\epsilon)$ equals, in the fine Markov partitions and long τ limits, with the sum of weights of form

$$w_{X,\tau} = \prod_{k=-\tau/2}^{\tau/2-1}\frac{1}{J^u(S^kX)} \tag{88}$$

of the cells containing the points X such that $e_\tau(X)$ lies in $B_{p,\epsilon}$. Then, denoting by $\pi_\tau(B_{p,\epsilon})$ the corresponding probability, one can write

$$\pi_\tau(e_\tau(X) \in B_{p,\epsilon}) \approx \frac{1}{M_\tau}\sum_{X:e_\tau(X)\in B_{p,\epsilon}} w_{X,\tau} \tag{89}$$

where M_τ is a normalization constant. *If the support of the physical measure is* $\mathcal{M}$, as in the case of moderate dissipation [27], time-reversibility and dissipation guarantee that the range of possible fluctuations includes a symmetric interval $[-p^*, p^*]$, with $p^* > 0$, and one can consider the ratio

$$\frac{\pi_\tau(B_{p,\epsilon})}{\pi_\tau(B_{-p,\epsilon})} \approx \frac{\sum\limits_{X,e_\tau(X)\in B_{p,\epsilon}} w_{X,\tau}}{\sum\limits_{X,e_\tau(X)\in B_{-p,\epsilon}} w_{X,\tau}}, \tag{90}$$

where each X in the numerator has a counterpart in the denominator. Denoting by I the involution which replaces the initial condition of a given trajectory with the initial condition of the reversed trajectory, time-reversibility yields:

$$\Lambda(X) = -\Lambda(IX), \quad w_{IX,\tau} = w_{X,\tau}^{-1} \quad \text{and} \quad \frac{w_{X,\tau}}{w_{IX,\tau}} = e^{-\tau\langle\Lambda\rangle p} \tag{91}$$

if $e_\tau(X) = p$. Taking small ϵ in $B_{p,\epsilon}$, the division of each term in the numerator of (90) by its counterpart in the denominator approximately equals $e^{-\tau\langle\Lambda\rangle p}$, which then equals the ratio in (90). Therefore, in the limit of small ϵ, infinitely fine Markov partitions and large τ, one obtains the following:

Gallavotti–Cohen Theorem. *Let* $(\mathcal{M}, S)$ *be dissipative and reversible and assume that the chaotic hypothesis holds. Then, in the* $\tau \to \infty$ *limit, one has*

$$\frac{\pi_\tau(B_{p,\epsilon})}{\pi_\tau(B_{-p,\epsilon})} = e^{-\tau\langle\Lambda\rangle p} \tag{92}$$

with an error in the argument of the exponential which can be estimated to be p- and τ*-independent.*

If Λ can be identified with a physical observable, the Λ-FR is a parameter-free statement about the physics of nonequilibrium systems. Unfortunately, Λ differs from the dissipated power in general, [28], hence alternative approaches have been developed.

5.2. Fluctuation Relations for the Dissipation Function

One different approach from above consists in posing a different question in order to remain closer to the interest of physics: if the FR has been observed to hold for the energy dissipation of a given system, which mechanisms are responsible for that? To answer this question, various results have been achieved and others clarified. In particular:

1. transient, or ensemble, FRs have been derived;
2. classes of infinitely many identities have been obtained to characterize equilibrium and nonequilibrum states;
3. a novel ergodic notion, known as *t-mixing*, has been introduced;
4. a quite general response formula has been derived.

These developments began with a paper by Evans and Searles [29], who proposed the first transient fluctuation relation for the *Dissipation Function* Ω, which is formally similar to Eq. (84). In states close to equilibrium, Ω can be identified with the *entropy production rate*, $\sigma = JVF^{ext}/k_BT$, where, J is the (intensive) flux due to the thermodynamic force F^{ext}, V and T are the volume and the kinetic temperature, respectively [29,30]. This relation, called transient Ω-FR, is obtained under virtually no hypothesis, except for *time reversibility*; it is transient because it concerns non-invariant ensembles of systems, instead of the steady state. The approach stems from the belief that the complete knowledge of the invariant measure implied by the Chaotic Hypothesis is not required to understand the few properties of physical interest, like thermodynamic relations do not depend on the details of the microscopic dynamics [31].

Let $\mathcal{M}$ be the phase space of the system at hand, and $S^\tau : \mathcal{M} \to \mathcal{M}$ be a reversible evolution corresponding to $\dot\Gamma = F(\Gamma)$. Take a probability measure $d\mu_0(\Gamma) = f_0(\Gamma)d\Gamma$ on $\mathcal{M}$, and let the observable $\mathcal{O} : \mathcal{M} \to I\!R$ be odd with respect to the time reversal, *i.e.* $\mathcal{O}(I\Gamma) = -\mathcal{O}(\Gamma)$. Denote its time averages by

$$\overline{\mathcal{O}}_{t,t+\tau}(\Gamma) \equiv \frac{1}{\tau}\mathcal{O}_{t_0,t_0+\tau}(\Gamma) \equiv \frac{1}{\tau}\int_{t_0}^{t_0+\tau}\mathcal{O}(S^s\Gamma)ds. \tag{93}$$

For a density f_0 that is even under time reversal $[f_0(I\Gamma) = f_0(\Gamma)]$, define the

Dissipation Function:

$$\Omega(\Gamma) = -\frac{d}{d\Gamma}\ln f_0\Big|_\Gamma \cdot \dot\Gamma - \Lambda(\Gamma), \quad \text{so that} \tag{94}$$

$$\overline{\Omega}_{t,t+\tau}(\Gamma) = \frac{1}{\tau}\left[\ln\frac{f_0(S^t\Gamma)}{f_0(S^{t+\tau}\Gamma)} - \Lambda_{t,t+\tau}\right] \tag{95}$$

For a compact phase space, the uniform density $f_0(\Gamma) = 1/|\mathcal{M}|$ implies $\Omega = \Lambda$, which was the case of the original FR. The existence of the logarithmic term in (94) is called *ergodic consistency*, a condition met if $f_0 > 0$ in all regions visited by all trajectories $S^t\Gamma$.

For $\delta > 0$, let $A_\delta^\pm = (\pm A - \delta, \pm A + \delta)$, and let $E(\mathcal{O} \in (a,b))$ be the set of points Γ such that $\mathcal{O}(\Gamma) \in (a,b)$. Then, we have $E(\overline{\Omega}_{0,\tau} \in A_\delta^-) = IS^\tau E(\overline{\Omega}_{0,\tau} \in A_\delta^+)$ and:

$$\frac{\mu_0(E(\overline{\Omega}_{0,\tau} \in A_\delta^+))}{\mu_0(E(\overline{\Omega}_{0,\tau} \in A_\delta^-))} = \frac{\int_{E(\overline{\Omega}_{0,\tau} \in A_\delta^+)} f_0(\Gamma)d\Gamma}{\int_{E(\overline{\Omega}_{0,\tau} \in A_d^+ elta)} f_0(S^\tau X)e^{-\Lambda_{0,\tau}(X)}dX}$$

$$= \frac{\int_{E(\overline{\Omega}_{0,\tau} \in A_\delta^+)} f_0(\Gamma)d\Gamma}{\int_{E(\overline{\Omega}_{0,\tau} \in A_\delta^+)} e^{-\Omega_{0,\tau}(X)} f_0(X)dX} = \langle e^{-\Omega_{0,\tau}}\rangle^{-1}_{\overline{\Omega}_{0,\tau} \in A_\delta^+}$$

where by $\langle\cdot\rangle_{\overline{\Omega}_{0,\tau} \in A_\delta^+}$ we mean the average computed with respect to μ_0 under the condition that $\overline{\Omega}_{0,\tau} \in A_\delta^+$. This implies the

Transient Ω-FR:

$$\frac{\mu_0(E(\overline{\Omega}_{0,\tau} \in A_\delta^+))}{\mu_0(E(\overline{\Omega}_{0,\tau} \in A_\delta^-))} = e^{[A+\epsilon(\delta,A,\tau)]\tau}, \tag{96}$$

with $|\epsilon(\delta, A, \tau)| \leqslant \delta$, an error due to the finiteness of δ.

Remark.

- **i.** The transient Ω-FR refers to the non-invariant probability distribution μ_0. Time reversibility is basically the only ingredient of its derivation.
- **ii.** Its similarity with the steady state FR is misleading: rather than expressing a statistical property of fluctuations of a given system, it expresses a property of the initial ensemble of macroscopically identical systems.
- **iii.** In order for Ω to be the energy dissipation, f_0 has to be properly chosen. For instance, in simple molecular dynamics models, Ω is the energy dissipation if f_0 is the equilibrium ensemble dynamics, which is obtained when the external driving is switched off, while the thermostats keep acting.
- **iv.** Consequently, *the transient Ω-FR yields a property of the equilibrium state by means of nonequilibrium experiments*, thus complementing the FDR, which yields non equilibrium properties from equilibrium experiments.

The steady state Ω-FR requires further hypotheses. In the first place let averaging begin at time t, i.e. consider

$$\frac{\mu_0(E(\overline{\Omega}_{t,t+\tau} \in A_\delta^+))}{\mu_0(E(\overline{\Omega}_{t,t+\tau} \in A_\delta^-))}. \tag{97}$$

Taking $\hat{t} = t + \tau + t$, the transformation $\Gamma = IS^{\hat{t}}W$ in $\mathcal{M}$ and some algebra yield:

$$\frac{\mu_0(E(\overline{\Omega}_{t,t+\tau} \in A_\delta^+))}{\mu_0(E(\overline{\Omega}_{t,t+\tau} \in A_\delta^-))} = \langle\exp\left(-\Omega_{0,\hat{t}}\right)\rangle^{-1}_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+} \tag{98}$$

$$= e^{[A+\epsilon(\delta,t,A,\tau)]\tau}\langle e^{-\Omega_{0,t}-\Omega_{t+\tau,2t+\tau}}\rangle^{-1}_{\overline{\Omega}_{t,t+\tau \in A_\delta^+}} \tag{99}$$

where $|\epsilon(\delta, t, A, \tau)| \leqslant \delta$. Here, the second line follows from the first because $\Omega_{0,\hat{t}} = \Omega_{0,t} + \Omega_{t,t+\tau} + \Omega_{t+\tau,\hat{t}}$, with the central contribution made approximately equal to A by the condition $\overline{\Omega}_{t,t+\tau} \in A_\delta^+$. Recall that $\mu_0(E) = \mu_t(S^tE)$, where μ_t is the evolved probability distribution, with density f_t. Then, taking the logarithm and dividing by τ Eq. (99) produces:

$$\frac{1}{\tau}\ln\frac{\mu_t(E(\overline{\Omega}_{0,\tau} \in A_\delta^+))}{\mu_t(E(\overline{\Omega}_{0,\tau} \in A_\delta^-))} = A + \epsilon(\delta,t,A,\tau) - \frac{1}{\tau}$$

$$\times \ln\langle e^{-\Omega_{0,t}-\Omega_{t+\tau,2t+\tau}}\rangle_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+}$$

$$\equiv A + \epsilon(\delta,t,A,\tau) + M(A,\delta,t,\tau) \tag{100}$$

because $E(\overline{\Omega}_{0,\tau}) = S^tE(\overline{\Omega}_{t,t+\tau})$.

If μ_t tends to a steady state μ_∞ when $t \to \infty$, the exact relation (100) changes from a statement on the ensemble f_t, to a statement on the statistics generated by a single typical trajectory. In particular one could have the analogous of the Λ-FR:

Steady State Ω-FR. For any tolerance $\epsilon > 0$, there is a sufficiently small $\delta > 0$ such that

$$\lim_{\tau\to\infty}\frac{1}{\tau}\ln\frac{\mu_\infty(E(\overline{\Omega}_{0,\tau} \in A_\delta^+))}{\mu_\infty(E(\overline{\Omega}_{0,\tau} \in A_\delta^-))} = A + \eta, \quad \text{with} \quad \eta \in (-\epsilon, \epsilon) \tag{101}$$

For this to be the case, one needs some assumption. Indeed, $M(A,\delta,t,\tau)$ could diverge with t at fixed τ, making Eq. (100) useless. If on the other hand $M(A,\delta,t,\tau)$ remains bounded by a finite $M(A,\delta,\tau)$, $\lim_{\tau\to\infty}M(A,\delta,\tau)$ could still exceed ϵ.

The first difficulty is simply solved by the observation that the divergence of $M(A,\delta,t,\tau)$ implies that one of the probabilities on the left hand side of Eq. (100) vanishes, i.e./ that A or $-A$ are not observable in the steady state. If no value A is observable, there are no fluctuations in the steady state and there is no need for a steady state FR. Therefore, let us assume that A and $-A$ are observable. To proceed, observe that Eqs. (94) and (95) lead to

$$f_s(\Gamma) = f_0(S^{-s}\Gamma)e^{-\Lambda_{-s,0}(\Gamma)} = f_0(\Gamma)e^{\Omega_{-s,0}(\Gamma)} \tag{102}$$

which implies the following relation:

$$\langle e^{-\Omega_{0,s}}\rangle_0 = 1, \quad \text{for every } s \in I\!R. \tag{103}$$

Suppose now that the Ω-autocorrelation with respect to f_0 decays instantaneously in time, so that one can write:

$$1 = \langle e^{-\Omega_{0,s}-\Omega_{s,t}}\rangle_0 = \langle e^{-\Omega_{0,s}}\rangle_0\langle e^{-\Omega_{s,t}}\rangle_0, \tag{104}$$

hence

$$\langle e^{-\Omega_{s,t}}\rangle_0 = 1, \quad \text{for all } s \text{ and } t \tag{105}$$

under the same condition, the conditional average of Eq. (100) does not depend on the condition $\overline{\Omega}_{t,t+\tau} \in A_\delta^+$, so that:

$$\langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}}\rangle_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+} = \langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}}\rangle_0 = 1. \tag{106}$$

Then, the logarithmic correction in Eq. (100) identically vanishes for all t, τ, and the steady state Ω-FR is verified at all $\tau > 0$. This idealized situation does not need to be realized, but molecular dynamics indicates that the typical situation is similar to this [32]; for τ much larger than a characteristic time τ_M, one may write:

$$\langle e^{-\Omega_{0,t}} \cdot e^{-\Omega_{t+\tau,2t+\tau}} \rangle_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+} \approx \tag{107}$$

$$\approx \langle e^{-\Omega_{0,t-t_M}} \cdot e^{-\Omega_{t+\tau+t_M,2t+\tau}} \rangle_{\overline{\Omega}_{t,t+\tau} \in A_\delta^+} \tag{108}$$

$$\approx \langle e^{-\Omega_{0,t-t_M}} \cdot e^{-\Omega_{t+\tau+t_M,2t+\tau}} \rangle_0 \tag{109}$$

$$\approx \langle e^{-\Omega_{0,t+t_M}} \rangle_0 \langle e^{-\Omega_{t+\tau+t_M,2t+\tau}} \rangle_0 = O(1), \tag{110}$$

with improving accuracy for growing t and τ. If these scenarios are realized, $M(A, \delta, \tau)$ vanishes as $1/\tau$ for growing τ.

The assumption that Eqs. (107)–(110) hold is a kind of mixing property which, however, refers to non-invariant probability distributions, differently from the standard notion of mixing.

Various other relations can be obtained following the same procedure. For instance, for each odd $\mathcal{O}$, any $\delta > 0$, any t and any τ the following transient FR holds:

$$\frac{\mu_0(\overline{\mathcal{O}}_{0,\tau} \in A_\delta^+)}{\mu_0(\overline{\mathcal{O}}_{0,\tau} \in A_\delta^-)} = \langle \exp(-\Omega_{0,\tau}) \rangle^{-1}_{\overline{\mathcal{O}}_{0,\tau} \in A_\delta^+}, \tag{111}$$

expressed a property of the initial state by means of non-equilibrium dynamics.

6. *t*-Mixing and general response theory

Observing that Eq. (30), implies:

$$\langle e^{-\Omega_{s,t}} \rangle_0 = \langle e^{-\Omega_{0,t-s}} \rangle_s \tag{112}$$

Eqs. (107)–(110) appear to be one special case of the following property:

$$\lim_{t \to \infty} \left[\langle \psi(\phi \circ S^t) \rangle_0 - \langle \psi \rangle_0 \langle \phi \rangle_t \right] = 0 \tag{113}$$

In the case that $\psi = \Omega$, Eq. (113) becomes

$$\lim_{t \to \infty} \langle \Omega(\phi \circ S^t) \rangle_0 = 0 \tag{114}$$

because Ω is odd and f_0 is even under time reversal, hence $\langle \Omega \rangle_0 = 0$.

If the convergence of this limit is faster than $O(1/t)$, one further has:

$$\int_0^\infty \langle \Omega(\phi \circ S^t) \rangle_0 \mathrm{d}t \in \mathbb{R} \tag{115}$$

a condition which has been called *t-mixing*.

To obtain the response of observables, starting from an equilibrium state, we have:

$$\langle \phi \rangle_t - \langle \phi \rangle_0 = \int_0^t \frac{\mathrm{d}}{\mathrm{d}s} \langle \phi \rangle_s \mathrm{d}s = \int_0^t \mathrm{d}s \frac{\mathrm{d}}{\mathrm{d}s} \int \mathrm{d}\Gamma f_s(\Gamma) \phi(\Gamma) \tag{116}$$

Where Eq. (102) yields:

$$\frac{\mathrm{d}}{\mathrm{d}s} \int \mathrm{d}\Gamma f_s(\Gamma) \phi(\Gamma) = \int \mathrm{d}\Gamma f_0(\Gamma) e^{\Omega_{-s,0}(\Gamma)} \Omega(S^{-s}\Gamma) \phi(\Gamma) \tag{117}$$

Introducing the coordinate change $X = S^{-s}\Gamma, \Gamma = S^s X$, with Jacobian determinant $|\partial\Gamma/\partial X| = \exp(\Lambda_{0,s}(X)$ and observing that:

$$\begin{aligned} \Omega_{-s,0}(S^s X) &= \int_{-s}^0 \mathrm{d}u \Omega(S^u S^s X) = \int_0^s \mathrm{d}z \Omega(S^z X) \\ &= \Omega_{0,s}(X) \end{aligned} \tag{118}$$

so we finally obtain:

$$\frac{\mathrm{d}}{\mathrm{d}s} \langle \phi(\Gamma) \rangle_s = \int \mathrm{d}X \phi(S^s X) \Omega(X) e^{\Omega_{0,s}(X)} e^{\Lambda_{0,s}(X)} f_0(S^s X) \tag{119}$$

$$= \int \mathrm{d}X \Omega(X) \phi(S^s X) f_0(X) = \langle \Omega(\phi \circ S^s) \rangle_0 \tag{120}$$

which is the integrand of Eq. (115). Therefore, we have the following Response Formula:

$$\langle \phi \rangle_t = \langle \phi \rangle_0 + \int_0^t \mathrm{d}s \langle \Omega(\phi \circ S^s) \rangle_0 \tag{121}$$

Moreover, if the t-mixing condition holds for ϕ, we get

$$\langle \phi \rangle_t \xrightarrow{t \to \infty} \langle \phi \rangle_0 + \int_0^\infty \mathrm{d}s \langle \Omega(\phi \circ S^s) \rangle_0 \in \mathbb{R} \tag{122}$$

and the ensemble under investigation converges to what appears to be a steady state.

One interesting aspect of the relation between standard mixing and t-mixing is the following. Standard mixing concerns the decay of correlations among the evolving microscopic phases within a given steady state, t-mixing concerns the decay of correlations among evolving macrostates. For this reason, the t-mixing property implies the convergence to a steady state, whereas the mixing property in general does not.

Mixing assumes the state to be stationary, making irrelevant the issue of relaxation. The derivation of convergence to a microcanonical state, illustrated in Section 2.1, is thus just a trick. That derivation is possible because one may formally interpret the evolving transient probability densities as evolving *observables* as well. This way one combines in one mathematical object two physically very different entities: the ensemble of microscopic phases and a macroscopic measurable observable.[8] This will not be legitimate under most circumstances. However, even in the case of t-mixing, the convergence of the steady state has not been proved in the sense of thermodynamics. Indeed, different initial conditions $\Gamma \in \mathcal{M}$ are allowed by t-mixing to produce different time averages. The uniqueness of the time average is currently under investigation.

7. Stochastic diffusions and large deviations

Let us now turn our attention to stochastic dynamics. In general, the presence of noise allows one to characterize the steady state dynamics, even in presence of dissipation, by regular probability densities, thus overcoming the problem posed e.g. by fractal structures. Hence, one may safely rely, in this case, on perturbative approaches in the

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[8] Something similar happens when the equilibrium thermodynamic entropy of a physical object is expressed by the equilibrium average of the logarithm of the equilibrium density, which is the Gibbs entropy.

description of perturbations of a given (possibly dissipative) reference state. In particular, a detailed analysis of the response formulae valid for Markovian Langevin-type stochastic differential equations is presented in Ref. [33], where Ruelle clarifies the conditions under which the zero noise limit leads the various terms of the perturbation theory to reproduce theie counterparts in the deterministic dynamics, cf. Refs. [34,35]. In Ruelle's case, this is made possible by the stability of the SRB states under small random perturbations [36–38].

A different approach based on the large deviations method is presented in Refs. [39,40]. Let us focus, for simplicity, on stochastic diffusion processes described by overdamped Langevin equations, in which one disregards inertial effects, letting forces to be proportional to velocities rather than to accelerations [41,42]. These processes correspond to the high damping limits of the underdamped (or *inertial*) stochastic dynamics. Let us start considering overdamped diffusion processes for $x \in \mathbb{R}^n$, in the Itô sense expressed by:

$$\dot{x}_t = \chi \cdot [F(x_t) + F_t^p(x_t)] + \nabla \cdot D(x_t) + \sqrt{2D(x_t)}\,\xi_t, \tag{123}$$

where ξ_t denotes standard white noise and F_t^p denotes the perturbation to the reference dynamics. The mobility χ and the diffusion constant D are strictly positive (symmetric) $n \times n$-matrices, which, provided the system is in contact with a thermostat at inverse temperature $\beta > 0$, are connected by the Einstein relation $\chi = \beta D$. The force F denotes the drift of the reference unperturbed dynamics, and can be expressed as:

$$F = F_{nc} - \nabla U, \tag{124}$$

where F_{nc} denotes a nonconservative force pulling the reference dynamics out of equilibrium, while U is the energy of the system. The Fokker–Planck equation for the time dependent density f_t, related to the diffusion process described by (123), reads

$$\frac{\partial f_t}{\partial t}(x_t) = -\nabla \cdot j_f, \quad \text{with} \quad j_f = [\chi(F + F_t^p) f_t(x_t) - \frac{\chi}{\beta}\nabla f_t(x_t)], \tag{125}$$

where j_f denotes the probability current [43]. Rather than attempting a direct solution of Eq. (125), one may tackle Eq. (123) from the point of view of large deviations theory [39,44]. The key idea, cf. Refs. [39,46], is to determine the perturbed probability density through its embedding in the path-space distribution. That is, given the (random) paths $\omega = (x(s), s \in [0,t])$, one may connect the distribution P on paths starting from f_0 and subjected to the perturbation F_t^p, with the reference distribution P^o pertaining to paths starting from f_0 and undergoing the reference dynamics, via the formula:

$$P(\omega) = e^{-\mathcal{A}(\omega)} P^o(\omega). \tag{126}$$

The relation (126) defines the action $\mathcal{A}(\omega)$, which is typically local in space–time and is, thus, similar to the Hamiltonians or Lagrangians of equilibrium statistical mechanics, see e.g. [47]. One can also decompose, in terms of its time symmetric components t and its time antisymmetric components:

$$\mathcal{A} = (\mathcal{T} - S)/2,$$

where

$$S(\omega) = \mathcal{A}(g\omega) - \mathcal{A}(\omega), \quad \mathcal{T}(\omega) = \mathcal{A}(g\omega) + \mathcal{A}(\omega). \tag{127}$$

and g is the time reversal operator:

$$g\omega = ((\pi x)_{t-s}, 0 \leqslant s \leqslant t), \tag{128}$$

with πx equal to x except for flipping any other variable with negative parity under time reversal. The quantity $S(\omega)$, under the assumption of local detailed balance [45], is the entropy flux triggered by the perturbation and released into the environment [39]. On the other hand, the quantity $\mathcal{T}(\omega)$ is referred to, in the literature, as *dynamical activity* [41,42], as it measures the reactivity and instability of a trajectory. Dynamical activity is thus much more concerned with kinetics than with thermodynamics but it allows us to explore response around equilibrium beyond the linear regime. This shows also that the noise along in- and outgoing trajectories is crucial for the determination of state plausibilities [48–50].

A simple calculation yields the following general expression for the action pertaining to the process described by Eq. (123):

$$\mathcal{A}(\omega) = \frac{\beta}{2}\int_0^t ds\left[F_s^p \cdot \chi F + \nabla \cdot (DF_s^p) + \frac{1}{2} F_s^p \cdot \chi F_s^p\right] - \frac{\beta}{2}\int_0^t dx_s \circ F_s^p \tag{129}$$

where the stochastic integral with the $\circ$ is in the sense of Stratonovich. From (127) and (129), one can derive the following expressions for $S(\omega)$ and $\mathcal{T}(\omega)$:

$$S(\omega) = \beta \int_0^t dx_s \circ F_s^p \quad \text{and} \quad \mathcal{T}(\omega) = \mathcal{T}_1 + \mathcal{T}_2,$$

with

$$\mathcal{T}_1 = \beta \int_0^t ds[F_s^p \cdot \chi F + \nabla \cdot (DF_s^p)] \quad \text{and} \quad \mathcal{T}_2 = \frac{\beta}{2}\int_0^t ds F_s^p \cdot \chi F_s^p.$$

If the chosen observable ϕ is endowed with an even kinematical parity, the following linear response formula can be thus established [41]:

$$\langle\phi\rangle_t - \langle\phi\rangle_0 \simeq \langle\phi(x_t)S(\omega)\rangle_0 = -\langle\phi(x_0)S(\omega)\rangle_0 = -\int dx_0 f_0(x_0)\phi(x_0)\langle S(\omega)\rangle_0^{x_0}. \tag{130}$$

The expression (130) looks similar to the response formula (121) obtained for deterministic systems, with the entropy flux $S(\omega)$ taking the role of the observable Ω defined in Eq. (94).[9] The quantity $\langle S\rangle_0^{x_0}$, in Eq. (130), denotes the conditional expectation of the entropy flux $S(\omega)$ over $[0,t]$

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[9] This is not surprising and indeed it is common. The fact is that both derivation are very formal and general and only the evolution operators and the observables must appear.

given that the path started from the state x_0. Its instantaneous flux is defined as [39,46]:

$$\langle S\rangle_0^{x_0} = \beta \int_0^t \langle w(x_s)\rangle_0^{x_0} ds, \tag{131}$$

where $w(x_s)$ corresponds to the instantaneous (time-antisymmetric, random) work made by the perturbation F_t^p.

7.1. Nonequilibrium steady states

By setting $F_{nc} \neq 0$, in Eq. (123), one spoils the time-reversibility of the reference dynamics. Therefore, given enough time, the reference dynamics settles on a nonequilibrium steady state described by an invariant density f_0 (usually not known). In the steady state, one can use the definition of the probability current given in Eq. (125), to define the *information potential* $\mathcal{I}_f$ [40,51] as:

$$\mathcal{I}_f = -\nabla(\log f_0) = (\beta/\chi)u - \beta F, \tag{132}$$

where $u \equiv j_f/f_0$ denotes a probability velocity. From Eq. (132), the large deviations method detailed in Ref. [35] leads to the following general response function for non-equilibrium overdamped diffusion processes:

$$R(t-s) = \chi\langle\left[-\nabla\cdot F_s^p(x_s) + \mathcal{I}_f(x_s)\cdot F_s^p(x_s)\right]\phi(x_t)\rangle_0. \tag{133}$$

In particular, if the perturbation takes the (time-independent) gradient form $F^p = \nabla V$, an easy calculation yields:

$$\begin{aligned} R(t-s) &= \beta\langle(u(x_s)\cdot\nabla V(x_s))\phi(x_t)\rangle_0 \\ &\quad - \beta\langle LV(x_s)\phi(x_t)\rangle_0, \end{aligned} \tag{134}$$

with $L = \chi F\cdot\nabla + \chi/\beta\nabla^2$. Next, by using the adjoint generator[10] $L^* = L - 2u\cdot\nabla$, one can suitably cast Eq. (134) into the equivalent form [35]:

$$\begin{aligned} R(t-s) &= -\beta\langle(u(x_s)\cdot\nabla V(x_s))\phi(x_t)\rangle_0 + \beta\frac{d}{ds} \\ &\quad \times\langle\phi(x_t)V(x_s)\rangle_0. \end{aligned} \tag{135}$$

It is worth remarking that the function $u(x)$, in (132), is unknown in general. Nevertheless, Eq. (134) is relevant at a formal level, because it shows that the response function can be expressed in terms of a suitable correlation function computed wrt reference stationary density characterizing the nonequilibrium steady state.

One also readily notices that Eq. (135) produces the classical Kubo formula (48) for $F_{nc} = 0$ (i.e. $u = 0$) or when describing the response in a reference frame moving with drift velocity u.

8. Concluding remarks

We have summarised some of the main results of the theory of nonequilibrium systems. We emphasized the physical questions and mechanisms lying behind the formalism presenting the various results in their historical order. Research has, in fact, gradually moved from the analysis of equilibrium systems to dissipative ones, from the regime of small fluctuations to large deviations. Along this challenging route, we also stressed similarity and difference between the different mathematical frameworks. In particular we noted the reassuring fact that (microscopic) deterministic dynamics, discussed in Section 6, give rise to similar linear response formulae as those of the (mesoscopic) stochastic dynamics, reviewed in Section 7. The resulting thermodynamic behavior of the observable under consideration is indeed expected not to depend on the mathematical framework used in the modelling, as long as the different frameworks describe the same phenomena.

We reviewed the main aspects lying behind the Onsager–Machlup theory: we described the regime of small fluctuations and also clarified the main mathematical prerequisites and the physical mechanism underlying that framework. We also reviewed the theory of Fluctuation Relations, through the prism of the Gallavotti–Cohen theorem addressing the large deviations properties of the phase space contraction rate, and of the Evans–Searles result concerning the symmetry properties of the observable known as Dissipation Function.

Finally, we discussed the recently introduced t-mixing condition, which concerns the decay of macroscopic correlations with respect to the initial state, hence the relaxation to steady states and the response of ensembles of physical systems.

Thus, although a comprehensive understanding of the physics of nonequilibrium systems is still missing, we believe that a unifying framework is gradually emerging.

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[10] L^* is defined with the help of the stationary distribution f_0: for any two state functions a and b, L^* is such that $\int dx f_0(x)a(x)L^*b(x) = \int dx f_0(x)b(x)La(x)$. For detailed balance dynamics, in particular, one has $L^* = \pi L\pi$, where π flips the variables which are odd under time reversal.

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t-mixing: from fluctuation relations to response and irreversibility in MD

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ABSTRACT
This paper provides an introduction to the theory of steady-state fluctuation relations for molecular dynamics systems, that led to a general theory of response. The main ingredient of this theory is a new dynamical condition now known as t-mixing. We use such a condition to identify necessary and sufficient conditions for the relaxation to a steady state (whether equilibrium or not) of an ensemble of identical systems, as well as of a single system. This allows us to address the problem of the irreversibility of time reversal invariant (conservative as well as dissipative) particle systems.

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1. Introduction

Fluctuations play a fundamental role in statistical mechanics, at least since Einstein's work on the Brownian motion,[1] which introduced the first fluctuation–dissipation relation. This work was continued for decades by many authors, greatly advancing our understanding of equilibrium and nonequilibrium phenomena, and culminated with the Green and Kubo theory of linear response.[2–7]

The terminology 'Fluctuation Relation' (FR), became popular after Evans et al. [8] published a paper on the steady-state fluctuations of the entropy production rate σ in the isoenergetic SLLOD model of a 2-dimensional shearing fluid made of N interacting particles of equal mass m:

$$\begin{cases}\dot{\mathbf{q}}_i = \mathbf{p}_i/m + \mathbf{n}_x\gamma y_i\\ \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{n}_x\gamma p_{yi} - \alpha\mathbf{p}_i\end{cases}\qquad \alpha = \frac{-\gamma P_{xy}V}{\sum_{i=1}^{N}\mathbf{p}_i^2/m},\qquad i = 1,\dots,N \tag{1}$$

Here γ is the shear rate, $\mathbf{n}_x$ is the unit vector along the x direction, $\mathbf{F}_i$ is the force exerted by all other particles on particle i and α is the ergostatting term, obtained from Gauss' principle of least constraint, in order to keep the internal energy constant.

In 1994, a relation for fluctuations of σ in transient states was derived by Evans and Searles [9]. One year later, Gallavotti and Cohen obtained steady-state relations for the phase space volumes contraction rate, casting the heuristic ideas proposed in Ref. [8] within the mathematically rigorous framework of Anosov dynamical systems.[10]

The FRs comprise one of the few examples of an exact, general result obtained for nonequilibrium systems to date. The steady-state FRs describe the fluctuations of observables in nonequilibrium systems, extending Green–Kubo and Onsager relations to states that are far from equilibrium,[11–13] they provide information about nanoscale systems, and are related to the macroscopic irreversibility that emerges from time reversal invariant (TRI) dynamics.

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Furthermore, while the fluctuation dissipation relations obtain information about nonequilibrium properties of physical systems by means of equilibrium experiments, the transient FRs obtain information about equilibrium systems by means of nonequilibrium experiments, something useful when equilibrium cannot be hoped for.

For sake of simplicity, given the space $\mathcal{M}$ of all microscopic phases $(\mathbf{q}_1, \mathbf{q}_2, \dots, \mathbf{q}_N, \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ of one d-dimensional system of N particles, let us denote by $\Gamma \in \mathcal{M} \subset \mathbb{R}^n$ and $n = 2dN$ one such phase, and by

$$\dot{\Gamma} = G(\Gamma), \tag{2}$$

the equations of motion.[1]

Equation (1) not only dissipate energy through their ergostat, they are also TRI. This means there exists one operator i acting on $\mathcal{M}$ that, combined with the inversion of the time, leaves these equations invariant, and such that $i^2\Gamma = i\, i\Gamma = \Gamma$. Introducing the time evolution operator, $S^t : \mathcal{M} \to \mathcal{M}$, meaning that $S^t\Gamma$ is the point at time t along a phase space trajectory starting at $(\mathbf{q}_1 \dots \mathbf{p}_N) = \Gamma$, TRI also amounts to state that

$$S^t i\, \Gamma = i S^{-t}\, \Gamma, \quad \text{for all points } \Gamma \in \mathcal{M} \text{ and all times } t \in \mathbb{R} \tag{3}$$

As schematically illustrated in Figure 1, this property allows us to associate every phase space trajectory segment enjoying certain properties forward in time, with a conjugate *reverse* trajectory enjoying opposite properties in its forward evolution. Equation (1) are not invariant under the usual operation $i(\mathbf{q}, \mathbf{p}) = (\mathbf{q}, -\mathbf{p})$; they are invariant under the following operation [14]:

$$i(x, y, z, p^x, p^y, p^z) = (x, -y, z, -p^x, p^y, -p^z) \tag{4}$$

This suffices to associate any trajectory segment with another one having opposite properties. Thanks to dissipation and TRI in the isoenergetic SLLOD model, Evans, Cohen and Morriss proposed and verified the first steady-state FR, which was written as:

$$\frac{\mu_\ell}{\mu_{\ell^*}} = \exp\left[Nd\tau\overline{\alpha}_{\ell,\tau}\right] \tag{5}$$

where d is the dimension of space, ℓ and ℓ^* are conjugate segments of length τ that occur with probability μ_ℓ and μ_{ℓ^*} in the steady state and $\overline{\alpha}_{\ell,\tau}$ is the time average of α along segment ℓ.[2]

In the case in which the system represents a macroscopic object in local thermodynamic equilibrium, $\overline{\alpha}_{\ell,\tau}$ is proportional to the average entropy production rate along ℓ, in which case Equation (5) provides a justification of the second law of thermodynamics, within the class of NEMD models. The reason is that the argument of the exponential contains N, which is very large for a macroscopic object, as well as the observation time τ which is also very large in terms of microscopic time units. Consequently, negative dissipations, possible in a reversible framework, have a totally negligible probability. Furthermore, Equation (5) is parameter-free, exact, and quite general. As a matter of fact, it extends Onsager and Green–Kubo relations far from equilibrium.[11,13] These are some of the reasons why Equation (5) became immediately popular.

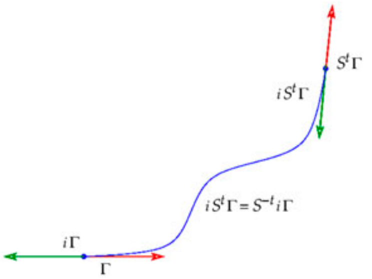

Figure 1. (Colour online) Represent a point $\Gamma = (\mathbf{q}, \mathbf{p})$ in phase space $\mathcal{M}$ by a point on a continuous line (position $\mathbf{q}$) together with an arrow (momentum $\mathbf{p}$). Let the initial point of a phase space trajectory segment be represented by the lowest point of the segment in the picture together with the arrow pointing to the right. Suppose the dynamics at hand is TRI, with time reversal operator i such that $i(\mathbf{q}, \mathbf{p}) = (\mathbf{q}, -\mathbf{p})$. Applying i to the initial Γ one obtains the same point at the bottom of the segment, with arrow pointing to the left. Evolving Γ for a time t, we obtain the final point of the trajectory segment, $S^t\Gamma$, which is the highest point in the segment, with arrow pointing upward. Applying i to this point, we turn downward the arrow of $S^t\Gamma$, obtaining $iS^t\Gamma$. This is the same as evolving the point $i\Gamma$ backward for a time t: $iS^t\Gamma = S^{-t}i\Gamma$. The trajectory segment starting at the point $iS^t\Gamma$ enjoys for a time t a dissipation opposite to that of the trajectory segment of duration t starting at Γ. Both segments proceed forward in time; only their initial conditions are different. Although the second of these initial conditions has been constructed using S^t and i, it remains one point, Γ' say, like any other phase in $\mathcal{M}$.

It was later realised that although fluctuations are not observed at the macroscopic level,[3] they are relevant in small systems, such as nanodevices and bio-physical systems.

The isoenergetic SLLOD system had been chosen by the authors of [8], because its phase space variation rate,

$$\Lambda = \operatorname{div} G \tag{6}$$

is proportional to α, and α is in turn proportional to the entropy production rate σ. [14–16] Then, using one expression for the steady-state probability distribution, obtained in the theory of Anosov systems,[17] eventually leading to Equation (5). Later, Equation (5) inspired the Gallavotti–Cohen Chaotic Hypothesis,[7,10,16] that was meant to justify and generalise the approach of Ref. [8]:

Chaotic Hypothesis: *A reversible N-particle system in a stationary state can be regarded as a transitive Anosov system, for the calculation of its macroscopic properties.*

This ambitious programme, explained at length in the literature, see e.g. the informative book [16], met some difficulties when applied to systems of physical interest, such as those of NEMD close to equilibrium, cf. Refs. [6,7,13,18]. Therefore, an alternative approach based on the theory of transient FR was developed.[18] Rather than asking which conditions are sufficient to obtain the steady-state FR for Λ, one may assume that the steady-state FR holds for the physical dissipation, because it is commonly verified, and then one may ask which conditions are necessarily verified in such a situation.[6] Indeed, sufficient conditions often entail unnecessary and even misleading ingredients, that are difficult to disentangle from the essential ones and that may overshadow the physically relevant mechanisms. Necessary conditions reveal instead aspects that are surely present when the phenomenon occurs, fostering our understanding. The present paper deals with advances made possible by this approach, whose main ingredient is the *t-mixing* condition.

The t-mixing condition has to be contrasted with the standard notion of *mixing*, which is a stronger property of dynamical systems than ergodicity is. These ergodic notions are typically assumed to hold (ergodic hypothesis), but the way they are formulated in the present mathematical literature make them too limited in scope, and not applicable to a sufficiently wide class of systems of physical interest. At the same time, the standard ergodic notions are too weak and do not capture fundamental aspects of physics such as the time scales.[19] In Appendix 1, we briefly recall the mathematical notions of ergodicity and mixing, within the scope of the present paper.

This paper is organised as follows. In Section 2, we introduce the dissipation function $\Omega^{(0)}$ and we present the derivation of the transient and steady-state fluctuations, showing that the steady-state FRs require the new dynamical condition known as t-mixing. In Section 3, we illustrate the notion of t-mixing showing its relevance for a totally general and exact response theory. In Section 4, we use t-mixing in order to cast a new light on the problem of irreversibility emerging from TRI dynamics. Section 5 contains our concluding remarks. Appendix 1 recalls ergodic notions. Appendix 2 shows that the dissipation function $\Omega^{(0)}$ represents indeed the physical dissipation.

Our main result, that profits from the analysis of Ref. [19], is that t-mixing implies irreversibility for the vast majority of phase space evolutions, whether the dynamics are conservative or dissipative. These kinds of arguments had been previously developed only for Hamiltonian dynamics.

2. From transient to steady-state FR

In order to identify the minimal ingredients that lead to the transient as well as to the steady-state FRs, it is most convenient to work in an abstract dynamical systems framework, in which two fundamental ingredients of NEMD models are present: dissipation and TRI. The concrete dynamics that one should keep in mind for simplicity are the Gaussian and Nosè–Hoover dynamics,[14,20] in the presence of constant boundary or bulk drivings. The equations of motion are then autonomous, and will be concisely written as in Equation (2). In this abstract setting we will define the observable $\Omega^{(0)}$, that should be thought of as the dissipative flux pertaining to the concrete dynamics at hand, cf. Appendix 2 below.

Let us denote by $S^t\Gamma$ the solution at time t of Equation (2) with initial condition Γ, for all times $t \in \mathbb{R}$. Let $\mathcal{O}$ be a real-valued function of phase. Performing a measurement of the macroscopic quantity associated with the microscopic property $\mathcal{O}$, we obtain the time average of $\mathcal{O}$ over an interval $[t, t+\tau]$ during which the measurement is taken:

$$\overline{\mathcal{O}}_{t,t+\tau}(\Gamma) := \frac{1}{\tau}\mathcal{O}_{t,t+\tau}(\Gamma) := \frac{1}{\tau}\int_t^{t+\tau}\mathcal{O}(S^s\Gamma)\mathrm{d}s. \qquad (7)$$

This quantity, with notation stressing that it is computed between the times t and $t+\tau$, depends on the initial phase Γ. Indeed, different initial phases result in different time evolutions, hence in different time averages. For fixed t and τ, the quantity $\overline{\mathcal{O}}_{t,t+\tau}$ is just another function of phase.

Let us now endow the phase space $\mathcal{M}$ with a probability distribution μ_0 of density f_0, so that the probability of a phase space volume element around Γ can be written as $\mathrm{d}\mu_0(\Gamma) = f_0(\Gamma)\mathrm{d}\Gamma$. The density f_0 may represent, for instance, an equilibrium state which, at some stage, is perturbed by dissipative forces. One may then ask what is the probability that in the initial state $\mathcal{O}$ takes values in the interval (a, b). By definition, this probability is obtained integrating $\mathrm{d}\mu_0$ over the set $\{\Gamma \in \mathcal{M} : \mathcal{O}(\Gamma) \in (a, b)\}$, denoted by $\mathcal{O}|_{(a,b)}$, i.e. over the phases Γ for which $\mathcal{O}(\Gamma)$ lies in (a, b):

$$\mu_0\left(\mathcal{O}|_{(a,b)}\right) = \int_{\mathcal{O}|_{(a,b)}} \mathrm{d}\mu_0(\Gamma) = \int_{\mathcal{O}|_{(a,b)}} f_0(\Gamma)\mathrm{d}\Gamma \qquad (8)$$

Let $(A)_\delta = (A-\delta, A+\delta)$. Then, the probability $\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta})$ that a measurement starting in the state described by f_0 yields within the time interval $[0, \tau]$ a value close to A with tolerance δ, is expressed by

$$\mu_0\left(\mathcal{O}_{0,\tau}|_{(A)_\delta}\right) = \int_{\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma.$$

The probability density f_0 and the phase space variation rate $\Lambda = \operatorname{div} G$ can be combined to define the phase variable known as Dissipation Function [6,21]:

$$\Omega^{(0)}(\Gamma) = -G(\Gamma)\cdot\frac{\mathrm{d}}{\mathrm{d}\Gamma}\ln f_0\bigg|_{\Gamma} - \Lambda(\Gamma) \qquad (9)$$

This requires f_0 to be *ergodically consistent* with the dynamics, i.e. f_0 has to be positive in all regions visited by the phase space trajectories $\{S^t\Gamma\}_{t\in\mathbb{R}}$. Although it may look an awkward phase variable, in the known cases $\Omega^{(0)}$ is the dissipation rate, provided f_0 equals the equilibrium distribution regarding the dynamics with the dissipative fields set to zero, cf. Appendix 2 and Refs. [6,18]. Averaging $\Omega^{(0)}$ along the trajectory starting at Γ, during the time interval $[t, t+\tau]$ yields:

$$\overline{\Omega}^{(0)}_{t,t+\tau}(\Gamma) = \frac{1}{\tau}\,\Omega^{(0)}_{t,t+\tau} = \frac{1}{\tau}\ln\frac{f_0(S^t\Gamma)}{f_0(S^{t+\tau}\Gamma)} - \overline{\Lambda}_{t,t+\tau}(\Gamma) \qquad (10)$$

2.1. Transient FR

For our TRI dynamics, let $\mathcal{O}$ be odd under time reversal, $\mathcal{O}(i\Gamma) = -\mathcal{O}(\Gamma)$, and consider the ratio of the μ_0-probability that $\overline{\mathcal{O}}_{0,\tau} \in (-A)_\delta$ to the μ_0-probability that $\overline{\mathcal{O}}_{0,\tau} \in (A)_\delta$:

$$\frac{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta})}{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta})} = \frac{\int_{\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma}{\int_{\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma}, \qquad (11)$$

To compute this quantity, which is reminiscent of the FR, observe that the phases in $\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta}$ are those, and only those, obtained from the points in $\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}$ as follows

$$\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta} = iS^\tau\,\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}. \qquad (12)$$

Therefore, the numerator of Equation (11) can be computed in terms of $\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}$, thanks to the coordinate transformation

$$\Gamma = iS^\tau X, \quad \text{whose Jacobian is} \quad J = \left|\frac{\mathrm{d}\Gamma}{\mathrm{d}X}\right| = e^{-\Lambda_{0,\tau}(X)}, \qquad (13)$$

where $\Lambda_{0,\tau}(X)$ is the integral of Λ along the trajectory from X to $S^\tau X$. Then,

$$\int_{\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma = \int_{\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}} f_0(iS^\tau X)\, e^{-\Lambda_{0,\tau}(X)}\mathrm{d}X \qquad (14)$$

In the case that f_0 is even under i, as in equilibrium states, $f_0(i\Gamma) = f_0(\Gamma)$, we eventually get:

Transient $\mathcal{O}$-FR:

$$\frac{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta})}{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta})} = \frac{\int_{\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}} f_0(S^\tau X)e^{-\Lambda_{0,\tau}(X)}\mathrm{d}X}{\int_{\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma}$$

$$:= \left\langle e^{-\Omega^{(0)}_{0,\tau}} \right\rangle^{(0)}_{\overline{\mathcal{O}}_{0,\tau}\in(A)_\delta}, \qquad (15)$$

Here, the last equality defines the conditional phase space average of $\exp(-\Omega^{(0)}_{0,t})$ with respect to μ_0, over the set of initial conditions such that $\overline{\mathcal{O}}_{r,s}(\Gamma) \in (A)_\delta$.[6,22]

In the case $\mathcal{O} = \Omega^{(0)}$, which is odd under i if f_0 is even, one obtains the elegant identity:

Transient Ω-FR:

$$\frac{\mu_0(\overline{\Omega}^{(0)}_{0,\tau}|_{(-A)_\delta})}{\mu_0(\overline{\Omega}^{(0)}_{0,\tau}|_{(A)_\delta})} = \left\langle \exp\left(-\Omega^{(0)}_{0,\tau}\right)\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{0,\tau}\in(A)_\delta} = e^{-[A+\epsilon(\delta,A,\tau)]\tau}, \qquad (16)$$

where the size of the correction term obeys $|\epsilon(\delta,A,\tau)| \le \delta$, because the conditional average is over the phase space trajectory segments in which the average of $\Omega^{(0)}$ lies within a distance δ from A.

Remarkably, the time-reversal invariance of the dynamics and of the probability density f_0 is the only ingredient of this derivation.

Note however that these transient relations are conceptually and also practically very different from the steady-state FR of [8]. Indeed, even for very large τ Equation (16) refers to the initial state characterised by μ_0 and not to the steady-state probability distribution which, as far as these relations are concerned, does not even need to exist. In other words, Equations (15) and (16) are called 'transient' because they use nonequilibrium dynamics to express properties of the initial state and not of the possible steady state. In this sense they close the circle with the fluctuation dissipation relations; these relations obtain nonequilibrium properties from equilibrium experiments, while the transient FRs obtain equilibrium properties from nonequilibrium experiments.

The transient FR differ from the steady-state FR also because they inherently concern ensembles of objects, or repetitions of the same experiment starting from different microscopic states but same macroscopic state. The steady-state FR do not need to concern ensembles, they can be verified in a single steady-state experiment, by observing the fluctuations in time of the observables of interest. Relations such as the Jarzynski equality lie in the class of transient FR.[7]

Given the dynamics S^t, different choices of f_0 are possible, hence different dissipation functions Ω and different transient FRs concerning different observables. For the interval $(-\delta,\delta)$, one obtains

$$\frac{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(-\delta,\delta)})}{\mu_0(\overline{\mathcal{O}}_{0,\tau}|_{(-\delta,\delta)})} = 1, \quad \text{hence} \quad \left\langle e^{-\Omega^{(0)}_{0,\tau}}\right\rangle^{(0)}_{\overline{\mathcal{O}}_{0,\tau}\in(-\delta,\delta)} = 1, \qquad (17)$$

which generalise the so-called nonequilibrium partition identity.[14] These identities have been used to test the accuracy of numerical simulations and to calibrate experimental equipment.[23]

2.2. Steady-state FR

To obtain the steady-state FRs, consider time averages starting at time $t > 0$, rather than at time 0, and consider the ratio

$$\frac{\mu_0(\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta})}{\mu_0(\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta})} = \frac{\int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma}{\int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma}. \qquad (18)$$

The phases concerning the numerator of Equation (18) are related to those concerning the denominator: $\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta} = iS^{2t+\tau}\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}$.[18] Therefore, introducing $X \in \mathcal{M}$ so that $\Gamma = iS^{2t+\tau}X$, we obtain

$$\int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta}} f_0(\Gamma)\mathrm{d}\Gamma$$

$$= \int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}} f_0(iS^{2t+\tau}X)e^{-\Lambda_{0,2t+\tau}(X)}\mathrm{d}X \qquad (19)$$

$$= \int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}} f_0(S^{2t+\tau}X)e^{-\Lambda_{0,2t+\tau}(X)}\mathrm{d}X \qquad (20)$$

$$= \int_{\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}} f_0(X)e^{-\Omega_{0,2t+\tau}(X)}\mathrm{d}X, \qquad (21)$$

thanks to the parity of f_0 and to Equation (10). The crucial difference from the case in which averaging starts at time 0, is that the coordinate transformation that links $\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta}$ to $\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}$ now requires a time longer than the averaging interval. The result is

$$\frac{\mu_0(\overline{\mathcal{O}}_{t,t+\tau}|_{(-A)_\delta})}{\mu_0(\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta})} = \left\langle \exp\left(-\Omega^{(0)}_{0,2t+\tau}\right)\right\rangle^{(0)}_{\overline{\mathcal{O}}_{t,t+\tau}\in(A)_\delta} \qquad (22)$$

where the right-hand side is the conditional average of $\exp(-\Omega^{(0)}_{0,2t+\tau})$, over phases Γ for which $\overline{\mathcal{O}}_{t,t+\tau}(\Gamma)$ is close to A. In the case that $\mathcal{O} = \Omega^{(0)}$, one obtains:

$$\frac{\mu_0(\overline{\Omega}^{(0)}_{t,t+\tau}|_{(-A)_\delta})}{\mu_0(\overline{\Omega}^{(0)}_{t,t+\tau}|_{(A)_\delta})}$$

$$= \left\langle e^{-\Omega^{(0)}_{0,t}}\ e^{-\Omega^{(0)}_{t,t+\tau}}\ e^{-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta} \qquad (23)$$

$$= e^{-\dagger A+\epsilon(\delta,t,A,\tau)\ddagger\tau}\left\langle e^{-\Omega_{0,t}}\ e^{-\Omega_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta} \qquad (24)$$

where the second equality follows because $\overline{\Omega}^{(0)}_{t,t+\tau}$ does not differ more than the accepted tolerance δ from A. Then, the error term ϵ depends in principle on δ, t, A and τ but is smaller than δ.

This result is exact, for all t, τ, δ, and for any A such that both probabilities $\mu_0(\overline{\Omega}^{(0)}_{t,t+\tau}|_{(-A)_\delta})$ and $\mu_0(\overline{\Omega}^{(0)}_{t,t+\tau}|_{(A)_\delta})$ are positive. Again, the only ingredient in this derivation is the time reversibility of the dynamics and of f_0. Moreover, Equations (22) and (24) are transient FRs, because they refer to the initial ensemble μ_0 for all t and τ.

We may now use the conservation of probability to replace the initial distribution μ_0 of density f_0, with the distribution μ_t of density f_t, which is produced evolving μ_0 for a time t:

$$\mu_t(S^t E) = \mu_0(E) \quad \text{i:e:} \int_{S^t E} f_t(X)\mathrm{d}X = \int_E f_0(X)\mathrm{d}X \qquad (25)$$

These equalities can be understood as follows. Consider a set of phases $E \subset \mathcal{M}$; in a time t each point Γ of E moves to another point, i.e. $S^t\Gamma$. Consequently, the set E turns the set S^tE moreover sets preserve in phase space their probability, like fluid volumes preserve their mass. The probability is then obtained integrating the corresponding probability density over each set of phases, like the mass is the integral of the density over the relevant volume.

To compute the probability density f_t, it suffices to introduce the coordinate transformation $Y = S^{-t}X$ and the corresponding Jacobian, in the left-hand side integral of Equation (25), [18]:

$$\left|\frac{\partial Y}{\partial X}\right| = e^{-\Lambda_{-t,0}(X)}, \quad f_t(X) = f_0(S^{-t}X)e^{-\Lambda_{-t,0}(X)}$$
$$= f_0(X)e^{-\Omega_{0,-t}(X)}. \qquad (26)$$

Observing that $S^t\overline{\mathcal{O}}_{t,t+\tau}|_{(a,b)} = \overline{\mathcal{O}}_{0,\tau}|_{(a,b)}$, one also has:

$$\mu_0(\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}) = \mu_t(S^t\overline{\mathcal{O}}_{t,t+\tau}|_{(A)_\delta}) = \mu_t(\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta}). \qquad (27)$$

and we may eventually rewrite Equation (18) as:

$$\frac{\mu_t(\overline{\mathcal{O}}_{0,\tau}|_{(-A)_\delta})}{\mu_t(\overline{\mathcal{O}}_{0,\tau}|_{(A)_\delta})} = \left\langle \exp\left(-\Omega^{(0)}_{0,2t+\tau}\right)\right\rangle^{(0)}_{\overline{\mathcal{O}}_{t,t+\tau}\in(A)_\delta} \qquad (28)$$

Like Equation (18), Equation (28) is exact and holds for all values t, τ, δ and for the appropriate values A. Furthermore, taking $\Omega^{(0)}$ in place of $\mathcal{O}$, Equation (28) implies:

$$\frac{\mu_t(\overline{\Omega}^{(0)}_{0,\tau}|_{(-A)_\delta})}{\mu_t(\overline{\Omega}^{(0)}_{0,\tau}|_{(A)_\delta})} = e^{-\tau\dagger A+\epsilon(\delta,t,A,\tau)\ddagger}\left\langle e^{-\Omega^{(0)}_{0,t}-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta} \qquad (29)$$

Now, let us assume that the distribution μ_t converges to a steady-state distribution μ_∞, i.e. that the probability $\mu_t(E)$ of any set of interest E in $\mathcal{M}$ tends to the steady-state probability $\mu_\infty(E)$, as $t \to \infty$. We may then investigate the $t \to \infty$ limit of Equation (29), in order to identify the conditions necessary for the steady-state FR to hold. To do that it is convenient to rewrite Equation (29) as follows:

$$\frac{1}{\tau}\ln\frac{\mu_t(\overline{\Omega}^{(0)}_{0,\tau}|_{(A)_\delta})}{\mu_t(\overline{\Omega}^{(0)}_{0,\tau}|_{(-A)_\delta})} = A + \epsilon(\delta,t,A,\tau) - \frac{1}{\tau}\ln\mathcal{C}_0(A,\delta,t,\tau), \qquad (30)$$

where we have introduced $\mathcal{C}_0$, a kind of auto-correlation function for the observable

$$\mathcal{Q}_t(\Gamma) := \exp\left[-\int_0^t \Omega^{(0)}(S^u\Gamma)\mathrm{d}u\right] \qquad (31)$$

that is defined by

$$\mathcal{C}_0(A,\delta,t,\tau) := \left\langle e^{-\Omega^{(0)}_{0,t}-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta}$$
$$= \left\langle \mathcal{Q}_t\left(\mathcal{Q}_t\circ S^{t+\tau}\right)\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta} \qquad (32)$$

where the composition of $\mathcal{Q}$ with the time evolution for a time $t+\tau$ means:

$$\left(\mathcal{Q}_t\circ S^{t+\tau}\right)(\Gamma) = \mathcal{Q}_t\left(S^{t+\tau}\Gamma\right)$$
$$= e^{-\int_0^t \Omega^{(0)}(S^uS^{t+\tau}\Gamma)\mathrm{d}u} = e^{-\int_{t+\tau}^{2t+\tau}\Omega^{(0)}(S^u\Gamma)\mathrm{d}u} \qquad (33)$$

As we are going to show, $\mathcal{C}_\prime$ is the paramount quantity of our theory. Its distinguishing feature is that it is computed with respect to the initial probability distribution μ_0, that is a transient distribution and depends neither on t nor on τ.

To obtain an expression valid in the steady state, the $t \to \infty$ limit has to be taken in Equation (30). To this end, let us introduce

$$M_0(A,\delta,\tau) := \frac{1}{\tau}\left|\limsup_{t\to\infty}\ \ln\mathcal{C}_0(A,\delta,\tau,t)\right|, \qquad (34)$$

which is an upper bound for the asymptotic values (as $t \to \infty$ at fixed A, δ, τ) of $\ln\mathcal{C}_0/\tau$. If M_0 diverges, one of the probabilities on the left-hand side of Equation (30) vanishes in the $t \to \infty$ limit, i.e. either A or $-A$ are not observable in the steady state. If no pair $(A, -A)$ is observable, there are no fluctuations in the steady state, hence the steady-state FR is of no interest. Conversely, if the steady-state FR holds, it means that there are observable pairs $(A, -A)$. We may then write

$$A - M_0(A,\delta,\tau) - \delta \le \frac{1}{\tau}\ln\frac{\mu_\infty(\overline{\Omega}^{(0)}_{0,\tau}|_{(A)_\delta})}{\mu_\infty(\overline{\Omega}^{(0)}_{0,\tau}|_{(-A)_\delta})}$$
$$\le A + M_0(A,\delta,\tau) + \delta \qquad (35)$$

If the steady-state FR holds for a value A of $\overline{\Omega}^{(0)}_{0,\tau}$, it means that, given any $\delta > 0$ the $\tau \to \infty$ limit of the central expression in Equation (35) remains within $[A-\delta, A+\delta]$, see e.g. Ref. [24, p.418]. This is the case if $M_0(A,\delta,\tau) \to 0$ as $\tau \to \infty$, i.e. if $\mathcal{C}_0$ does not grow exponentially fast with τ. Provided the initial distribution f_0 is the proper equilibrium one, we may then say that A and $-A$ are in the domain of the steady-state Ω-FR, i.e. of a FR for the physical dissipation.

3. t-mixing

What kind of condition is the convergence to zero of $M_0(A,\delta,\tau)$, when $\tau \to \infty$? Let us consider two extreme examples to understand that.

(a) Suppose the $\Omega^{(0)}$-autocorrelation computed with respect to the initial distribution decays instantaneously. Then also the correlations between exponentials of integrals of $\Omega^{(0)}$ decay instantaneously, and the conditional average in Equation (29) equals the unconditioned average:

$$\left\langle e^{-\Omega^{(0)}_{0,t}-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)}_{\overline{\Omega}^{(0)}_{t,t+\tau}\in(A)_\delta} = \left\langle e^{-\Omega^{(0)}_{0,t}-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)} \tag{36}$$

moreover, this average factorises:

$$\left\langle e^{-\Omega^{(0)}_{0,t}-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)} = \left\langle e^{-\Omega^{(0)}_{0,t}}\right\rangle^{(0)}\left\langle e^{-\Omega^{(0)}_{t+\tau,2t+\tau}}\right\rangle^{(0)} \tag{37}$$

Combining this result with Equation (17) with $\delta = \infty$, we can write

$$\begin{aligned} 1 = \left\langle e^{-\Omega^{(0)}_{0,t}}\right\rangle^{(0)} &= \left\langle e^{-\Omega^{(0)}_{0,s}}\, e^{-\Omega^{(0)}_{s,t}}\right\rangle^{(0)} \\ &= \left\langle e^{-\Omega^{(0)}_{0,s}}\right\rangle^{(0)}\left\langle e^{-\Omega^{(0)}_{s,t}}\right\rangle^{(0)}, \\ \text{hence } \left\langle e^{-\Omega^{(0)}_{s,t}}\right\rangle^{(0)} &= 1 \end{aligned} \tag{38}$$

for all s and t. Then, $\ln \mathcal{C}_0(A,\delta,\tau,t) = 0$ for all t and τ and the steady-state FR holds without any limit to be taken. As a matter of fact, an instantaneous decay of correlations implies immediate convergence to the steady state.

(b) Take one particle moving in empty space, under the action of a constant force $\mathbf{F}_e$ and a Gaussian isokinetic thermostat. The equations of motion are:

$$\dot{\mathbf{q}} = \mathbf{p}, \quad \dot{\mathbf{p}} = \mathbf{F}_e - \frac{\mathbf{F}_e\cdot\mathbf{p}}{\mathbf{p}\cdot\mathbf{p}}\mathbf{p}$$

If the initial momentum $\mathbf{p}$ points exactly in the direction opposite to $\mathbf{F}_e$, e.g. $\mathbf{p}(0) = -c\mathbf{F}_e$, with c any positive constant, $\mathbf{p}$ is a constant of the motion; analogously, $\mathbf{p}(0) = c\mathbf{F}_e$ is also a constant of the motion. All other initial conditions $\mathbf{p}(0)$ rapidly turn parallel to $\mathbf{F}_e$ keeping their magnitude. This dynamics has one repelling point, $-c\mathbf{F}_e$, and one attracting point, $c\mathbf{F}_e$. The attracting point $c\mathbf{F}_e$ is also the unique (stable) steady state; its probability distribution is the Dirac δ-function $\delta(\mathbf{p}-c\mathbf{F}_e)$, and obviously there are no fluctuations in this state. Therefore the steady-state FR does not hold. This is revealed in our theory by the fact that not only the correlations with respect to the initial distribution do not decay in the $t \to \infty$ limit: $\mathcal{C}$ actually grows exponentially fast with t, because $\Omega^{(0)}_{0,t}$ grows linearly with t.[4]

The above situations, one in which correlations with respect to f_0 decay instantaneously and the other in which they diverge exponentially fast, are clearly peculiar. Numerical simulations on NEMD systems indicate that typically $\mathcal{C}_0$ is bounded for a wide range of A values,[25] therefore the steady-state Ω-FR holds quite generally, with a correction of order $O(1/\tau)$, as expected on the grounds of the many numerical as well as experimental verifications of the steady state Ω-FR.

Now, the factorisation condition (37) appears to be one instance of the following property, that we call *t-mixing*:

$$\lim_{t\to\infty}\left[\left\langle \mathcal{O}\left(\mathcal{P}\circ S^t\right)\right\rangle^{(0)} - \langle\mathcal{O}\rangle^{(0)}\left\langle\mathcal{P}\circ S^t\right\rangle^{(0)}\right] = 0 \tag{39}$$

In particular, taking $\mathcal{O} = \Omega^{(0)}$, and recalling that $\langle\Omega^{(0)}\rangle^{(0)} = 0$, because $\Omega^{(0)}$ is odd for even f_0, Equation (39) becomes:

$$\lim_{t\to\infty}\left\langle \Omega^{(0)}\left(\mathcal{P}\circ S^t\right)\right\rangle^{(0)} = 0 \tag{40}$$

Let us express the evolution of phase space averages as follows:

$$\begin{aligned} \langle\mathcal{P}\rangle^{(t)} - \langle\mathcal{P}\rangle^{(0)} &= \int \mathcal{P}(\Gamma)\left[f_t(\Gamma) - f_0(\Gamma)\right]\mathrm{d}\Gamma \\ &= \int_0^t \frac{\mathrm{d}}{\mathrm{d}s}\langle\mathcal{P}\rangle^{(s)}\,\mathrm{d}s \\ &= \int_0^t \mathrm{d}s\frac{\mathrm{d}}{\mathrm{d}s}\int \mathrm{d}\Gamma f_s(\Gamma)\mathcal{P}(\Gamma) \end{aligned} \tag{41}$$

Using Equation (10), the coordinate transformation $\Gamma = S^sX$, with Jacobian determinant $|\partial\Gamma/\partial X| = \exp(\Lambda_{0,s}(X)$, and the fact that $\Omega^{(0)}_{-s,0}(S^sX) = \Omega^{(0)}_{0,s}(X)$ we eventually obtain:

$$\frac{\mathrm{d}}{\mathrm{d}s}\langle\mathcal{P}\rangle^{(s)} = \int \mathrm{d}X\,\Omega^{(0)}(X)\mathcal{P}\left(S^sX\right)f_0(X) = \left\langle\Omega^{(0)}\left(\mathcal{P}\circ S^s\right)\right\rangle^{(0)} \tag{42}$$

which also implies

$$\frac{\mathrm{d}}{\mathrm{d}t}\left\langle\Omega^{(0)}\right\rangle^{(0)}_t\Big|_{t=0} = \left\langle\Omega^{(0)}\,\Omega^{(0)}\right\rangle^{(0)} > 0. \tag{43}$$

Equation (43) requires f_t to be non-TRI in the first instants of its evolution, even if the evolution is dissipation-less, and converges to a different equilibrium state.

Thanks to Equation (42), the response Equation (41) can be rewritten as:

$$\langle\mathcal{P}\rangle^{(t)} = \langle\mathcal{P}\rangle^{(0)} + \int_0^t \mathrm{d}s\left\langle\Omega^{(0)}\left(\mathcal{P}\circ S^s\right)\right\rangle^{(0)} \tag{44}$$

This appears to be a fully general response formula, for an ensemble of identical systems, that start in the equilibrium state characterised by f_0 and then evolve under some perturbation codified by the evolution operator S^t. If the decay of ensemble averages (40) proceeds at a rate faster than $O(1/t)$, Equation (44) can be considered in the $t \to \infty$ limit:

$$\langle\mathcal{P}\rangle^{\infty} = \langle\mathcal{P}\rangle^{(0)} + \int_0^\infty \mathrm{d}s\left\langle\Omega^{(0)}\left(\mathcal{P}\circ S^s\right)\right\rangle^{(0)} \tag{45}$$

which expresses quite generally the asymptotic response of the initial ensemble to the driving.

The property that the integral in Equation (45) exists has recently been called 'Ωt-mixing'. Because it derives from a series of exact calculations without approximations, it is a necessary and sufficient condition for the response of an ensemble of systems. Equation (45) is exact, at variance with e.g. Green–Kubo linear response formula, which is valid 'only' to first order in the perturbation.

4. Irreversibility

In discussing the issue of irreversibility, we start from an obvious but important premise: we commonly understand the physical world in terms of mathematical models. These models embody the aspects we consider relevant for the phenomena of interest, and necessarily neglect other aspects.[26,27] Our expectations are thus quantitatively expressed and can be compared with empirical data. In this respect, statistical physics has been extremely successful since its very beginnings, thanks to informed choices that allow us to neglect large fractions of information on the enormous assemblies of interacting particles that constitute macroscopic objects.

That understanding may be fostered by loss of information is not strange; think e.g. of a movie: its frames pass rapidly before our eyes, and we are forced to neglect most of the information contained in them. For instance, we do not ponder at all the data regarding the pixels of each frame and the digitised sound, although that is the total information of which the movie is made. Nonetheless, deciding what is useful and what is to be neglected is far from obvious; in general, only experience can ultimately confirm or refute our assumptions. This endeavour is therefore particularly delicate when investigating aspects of the physical world that had not been considered before.

One should therefore bear in mind that all models are just that: they have a given range of applicability, delimited by certain space and time scales, because they have been devised to describe certain aspects of a given phenomenon and not others. This is true also for the microscopic dynamics that can be used to represent the atomic/molecular level of macroscopic systems, whose irreversibility is a well-established fact. In particular, the microscopic dynamics we commonly use have been successful in describing countless phenomena, but they could nevertheless be inappropriate to explain irreversibility.

As a matter of fact, almost any microscopic hypothesis implying macroscopic irreversibility is going to be consistent with observations, hence it is hard to experimentally select the correct one.[28,29] Classical examples of this are the equivalence of different formulations of quantum mechanics or of classical mechanics, such as Newton and Hertz mechanics. One may also recall the discussion on whether diffusion (arguably the simplest of irreversible phenomena) require microscopic chaos, in the sense of positive Lyapunov exponents.[30]

For these and many other reasons, irreversibility could be a physically irrelevant or ill-posed problem. Indeed, many doubts can be raised even about the most convincing explanations.[31–33]

The question remains intriguing because, as far as we know, the destiny of all what we see around us is essentially irreversible, hence a number of explanations of irreversibility have been proposed. In statistical physics, two main approaches have been developed [33]:

> Our choice of strategy boils down to either assuming temporally asymmetric boundary conditions or of adding (or changing to) time reversal noninvariant laws of nature that make entropy increase likely. Many approaches to this problem have thought to avoid this dilemma, but a little analysis of any proposed third way arguably proves this to be false.

We may conclude that the only sensible as well as safe statements that can be made on irreversibility concern the models at hand, i.e. models successful in answering certain questions, and capable of certain predictions, but whose applicability to the problem of irreversibility is still debatable. Among the models that are available, we find Hamiltonian particle systems relatively convincing for isolated systems, and we consider NEMD models suitable in the case of coupling with an external environment causing dissipation. In both cases, TRI holds.

4.1. Irreversible relaxation to equilibrium: the standard picture

Here we recall the approach based on Hamiltonian mechanics, meant to explain the irreversible convergence to equilibrium of an isolated system. The common example considered in this case is that of the expansion of a gas initially confined in one half of a container, or of the mixing of two liquids that are initially separated.

In this framework, irreversibility is justified by a combinatorial calculation, envisaged by Boltzmann and polished by subsequent authors, that profits from the enormous number of microscopic constituents of macroscopic objects. The reasoning tells that equilibrium states are so much more numerous than other states, that for a system evolving spontaneously through all kinds of states it is practically impossible to avoid equilibrium, except for rare and exceedingly short events.

Consider a discrete system with a finite number of states. For instance let a state be represented by a string of N symbols $X^{(N)} = (s_1, s_2, \ldots, s_N)$, each of which is drawn from a set $\mathcal{A} = \{\alpha_1, \alpha_2, \ldots, \alpha_L\}$. We may think of N as the number of particles, s_i as the state of particle i, e.g. its velocity, and $X^{(N)}$ as one microscopic phase of the system. The empirical distribution of the symbols in a given string may be viewed as one macrostate:

$$\nu\left(X^{(N)}\right) = \{\nu_1, \nu_2, \ldots, \nu_L\}$$

where ν_j is the frequency of symbol α_j in $X^{(N)}$. Depending on how many particles have certain velocities, the total kinetic energy takes a certain value. Different arrangements of particles lead to the same macrostate ν, and we may count how many such arrangements have same ν. Denote by

$$M(\nu) = \{X_1^{(N),\nu}, X_2^{(N),\nu}, \ldots, X_n^{(N),\nu}\}$$

the set of strings of N symbols with same empirical distribution ν. For instance, taking $\mathcal{A} = \{a, b\}$ and $N = 3$, the set of all possible phases contains 8 strings,

$$\mathcal{M} = \{aaa, aab, aba, baa, abb, bab, bba, bbb\},$$

the possible macrostates are 4:

$$\nu(aaa) = \{1, 0\}, \qquad \nu(bbb) = \{0, 1\}$$
$$\nu(aab) = \nu(aba) = \nu(baa) = \left\{\frac{2}{3}, \frac{1}{3}\right\},$$
$$\nu(abb) = \nu(bab) = \nu(bba) = \left\{\frac{1}{3}, \frac{2}{3}\right\},$$

two of which are given by a single arrangement, while the other two are each given in three different ways. One can show that the number of different macrostates is not larger than $(N+1)^L$, while the number of microstates equals L^N. Moreover, for sufficiently large N, the number of strings corresponding to a given empirical distribution ν is approximated by

$$W(\nu) = e^{NH(\nu)}, \text{ with } H(\nu) = -\sum_{j=1}^{L} \nu_j \ln \nu_j$$

Then, large N implies that the macrostate $\tilde{\nu}$ corresponding to the largest number of strings $\widetilde{W}$ contains by far the largest fraction of the total set of microscopic phases of $\mathcal{M}$, and dynamics jumping without constraints from string to string are bound to spend most of their time in $\tilde{\nu}$.[5]

These conclusions merely follow from *counting* microscopic phases. The above reasoning makes no reference to assumptions on the microscopic dynamics or on notions from probability theory. It simply states that it must be hard to avoid equilibrium states.

There is now a technical gap to overcome. The dynamics of particles occur in continuous time in a continuous space, rather than in discrete time and discrete space. This issue is usually overlooked, and counting of states is in this case replaced by comparing volumes in phase space. If a certain macrostate, e.g. a given distribution of mass, corresponds to a larger portion of phase space than another mass distribution, the first is considered realisable in more ways than the second. This approach has been criticised, but it is supported by some argument,[34] and in absence of better recipes it is commonly accepted.

Under these premises, the issue of irreversibility can be illustrated as in Figure 2. The phase space $\mathcal{M}$ of a system of N particles can be subdivided in regions that correspond to different values of a certain macroscopic observable F, with a tolerance j corresponding to the resolution of the measurement tools. The microscopic phases evolve drawing a line in $\mathcal{M}$. If N is small, various values of F occupy large regions of $\mathcal{M}$ and are observed with comparable frequency. If N is large by far the largest portion of $\mathcal{M}$ is occupied by the phases which we consider the equilibrium state. Observable fluctuations of F are rare and evanescent. Therefore, if the system starts, thanks to the experimentalist, in a region different from the equilibrium region, it rapidly reaches equilibrium and there it irreversibly sits. For N of order $O(10^{23})$, the fluctuations are so ridiculously rare that do not occur in the estimated lifetime of our universe,[35] cf. Figure 2. If the number of particles freely moving in a billiard table is 2, one cannot guess which picture has been taken first, Figure 3(a); but even for a moderately large numbers of particles the situation is immediately clear.

This is considered by many such an exceedingly simple and compelling argument, that they find incredible that the debate is still going on [35,36].

These qualitative results are rigorously formalised in the kinetic theory of rarefied gases, and go hand in hand with Khinchin's justification of the ergodic hypothesis.[37] As demonstrated numerically by Fermi, Pasta, Tsingou and Ulam and mathematically realised by Kolmogorov, Arnold and Moser, generically a Hamiltonian system is not ergodic. The ergodic hypothesis may nevertheless be adopted because physics concerns a few special observables, and because it deals with systems with very large N. The fact is that the fluctuations of the relevant observables are negligible; hence averaging these practically constant functions in time or in phase space necessarily yield indistinguishable results. More precisely, consider rarefied gases for which the Hamiltonian is approximately a sum of molecular contributions $H = \sum_{n=1}^{N} H_n(\mathbf{q}_n, \mathbf{p}_n)$, and introduce observables that can also be decomposed as sums of molecular contributions, as appropriate in this case for e.g. pressure and temperature:

$$F(\Gamma) = \sum_{n=1}^{N} F_n(\mathbf{q}_n, \mathbf{p}_n)$$

Then, applying the law of large numbers and considering the microcanonical ensemble, Khinchin obtains the following theorem [37]:

$$\text{Prob}\left(\frac{|\overline{F} - \langle F\rangle|}{|\langle F\rangle|} \geq K_1 N^{-1/4}\right) \leq K_2 N^{-1/4},$$

which states that the probability that the relative time average of F differs more than order $O\left(N^{-1/4}\right)$ from its microcanonical average, vanishes as $N^{-1/4}$. This is due to the fact that fluctuations become negligible as N grows, because sum variables are self-averaging. Whether the dynamics are technically ergodic or not is by and large irrelevant; what matters is the applicability of the law of large numbers.

There is one difficulty in this framework, if one wants to get to the root of the irreversible behaviour of all objects in the universe. As illustrated in Figure 2(b), a spontaneous evolution rapidly converges to the equilibrium state both forward and backward in time; it suffices to walk back on the line of the time evolution to see that. In Figure 3(b), if the ordered configuration of particles is the result of spontaneous evolution, the state would have been disordered even in the past. From this point of view, past and future are equivalent and no arrow of time can be identified.

Past and future are clearly distinguished only when a nonequilibrium state has been produced by someone or by some mechanism acting on a given object. Indeed, the reasons outlined above imply that a nonequilibrium state does not emerge from a spontaneous fluctuation: the probability that a spontaneous fluctuation results in a gas occupying half of a container or in a footprint on the sand is so ridiculously small that such an event is not expected to occur in a time such as the lifetime of the universe. If those phenomena have been observed, they must have been produced by someone or something. In turn, this someone or something do not emerge as spontaneous fluctuations; some other part of the universe must have acted in such a way to produce them. Eventually, in order to explain the arrow of time one is forced to consider the universe as a whole, and to assume that its initial state was very far from equilibrium.[38][6] Can such a special initial condition of the universe, from which all irreversibility derives, be justified? For different reasons, various authors claim that no justification is needed [33,39].

4.2. Concerns about the level of description required by the Hamiltonian picture

The theory outlined above relies on a relation between phase space volume and probability: a small fraction of the phase space

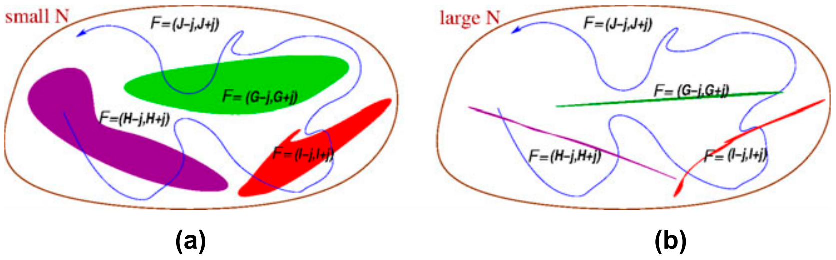

Figure 2. (Colour online) Standard argument for relaxation of a system made of many particles described by Hamiltonian dynamics, to an equilibrium state. One assumes that the dynamics explore without constraints the phase space $\mathcal{M}$, and that almost all the volume of $\mathcal{M}$ corresponds to equilibrium. Forward and backward in time, a phase space trajectory rapidly reaches equilibrium and stays there, apart from negligible deviations. (a) For small N the phase space is subdivided in regions of comparable size, in which a given observable F takes different values. Fluctuations of F are large and frequent. (b) large N, most of the phase space is occupied by phases in which F takes its mean value. Fluctuations are rare and evanescent.

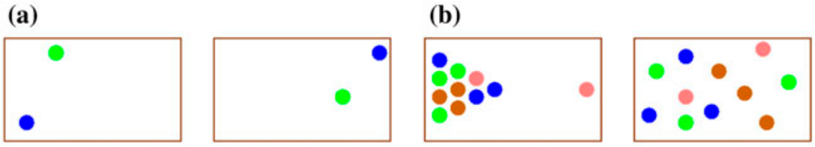

Figure 3. (Colour online) (a) For systems made of a few particles, no notion of disorder and of irreversibility make sense. Temporal sequences of spontaneously evolving systems cannot be inferred from observations. (b) Even for moderately large numbers of particles, sufficient for a notion of disorder to make sense, one guesses right away the correct sequence of events, under spontaneous evolution.

volume corresponds to a small probability, but as long as this volume is positive, the phases it contains will be experienced with given frequency. In this respect, Lebowitz's key statement is [35]: 'Unless there are reasons to the contrary (such as extra additive constants of the motion), the latter statement, a mild form of Boltzmann's ergodic hypothesis, seems very plausible for all macroscopic systems'. Here, extra additive constants of the motion represent just one kind of constraints that prevent the free exploration of the available phase space.[7] Because this picture is convincing for Hamiltonian dynamics, Lebowitz dismissed as unnecessary all other kinds of dynamics, such as those of NEMD mentioned by Hoover, Posch and Holian in a letter to the editors of Physics Today [40], motivated by Ref. [35].

These authors maintained that in NEMD stationary states:

> The nonequilibrium phase volume is completely negligible relative to the phase volume of the corresponding Gibbs's equilibrium ensemble –that with the same number of particles, same energy and same volume, but without the nonequilibrium fluxes. The negligible phase volume of the nonequilibrium states results from the multiplicity of constraints implicit in a steady state.

Lebowitz replied that [40]: 'So while it is interesting to speculate on what the world would look like with such dynamics, I believe it is confusing to bring them into the discussion of the conceptual problem of macroscopic irreversibility'.

Although the Hamiltonian theory discussed above looks at present the only one that can treat correctly at least one system of physical interest, it appears limited in scope and prohibitive to substantially extend beyond the rarefied gas.[8] Therefore, a different approach may prove beneficial because, as noted above, every model applies to certain phenomena, within certain space and time scales. In this respect, classical mechanics is nothing less than amazing; the extent of its applicability in science and technology cannot be overestimated. Nevertheless, Laplace daring statement:

> The regularity which astronomy shows us in the movements of the comets doubtless exists also in all phenomena. The curve described by a simple molecule of air or vapour is regulated in a manner just as certain as the planetary orbits; the only difference between them is that which comes from our ignorance [41, p.6], could be excessive.

Analogously, trust in the Hamiltonian formulation of classical mechanics could have been exaggerated by the success of quantum mechanics.

In the end, certain phenomena may be more economically described by non-Hamiltonian models, without making direct reference to the fundamental laws of physics.[9] In particular, 'it is interesting to speculate on what the world would look like with such dynamics', because Hamiltonian models force us to investigate such remote phenomena as the whole universe and its initial conditions, even when we only want to describe the most common feature of our daily life: dissipation.

Indeed, in the case of dissipative fields driving a system away from equilibrium, the observation made by Hoover, Posch and Holian holds independently of the dynamical model we choose. For instance, an electric field driving a current does so because it introduces constraints that limit the possible motions of the electrons, and fluctuations that are very rare in equilibrium become the average and typical value. These constraints are not like constants of the motion; they are much more subtle and complex. In particular, they are a reason of concern for the Hamiltonian theory, because, preventing the free motion in phase space, they frustrate the application of 'counting'.

One may insist that the problem is that we should consider the universe as a whole, and not just a part. Nevertheless, it seems legitimate to hold that the whole universe is way too cumbersome to handle, compared to an electric current in a wire, observed within human space and time scales. NEMD deals much more efficiently with that than a general theory of the evolution of the universe could possibly do. NEMD might therefore help in clarifying some aspects of irreversibility, even though it does not start from the fundamental forces of nature.

4.3. *t-mixing and single system relaxation: irreversibility*

Let us consider TRI dynamics, that may be or not be driven by a dissipative field. We intend to identify the conditions for relaxation to equilibrium or nonequilibrium steady states. In principle, we are not committed to NEMD models, but these are the ones that we trust in countless applications. As observed above, Ωt-mixing, i.e. the existence of the following integral

$$\int_0^\infty \mathrm{d}s \left\langle \Omega^{(0)} \left(\mathcal{P} \circ S^s\right)\right\rangle^{(0)} \qquad (46)$$

is necessary and sufficient for the relaxation of an ensemble of systems to a steady state. If the initial ensemble is properly chosen, relatively to the nonequilibrium dynamics S^t at hand, $\Omega^{(0)}$ is the corresponding energy dissipation, but one may also consider different initial ensembles and correspondingly different dissipation functions $\Omega^{(0)}$. Therefore, t-mixing avoids one problem of ergodic theory: the fact that ergodic theory concerns invariant states, hence that it offers limited information about relaxation of ensembles.

Relaxation in the sense of ensembles, is the standard result in response theory, although for one macroscopic object one would need a theory describing the behaviour of that single object. Ensemble results are commonly accepted under the assumption that ensembles express anyway the behaviour of single objects. In equilibrium, this view is relatively well justified by the theory of irreversibility illustrated above, since that theory guarantees that practically all systems, and not just an abstract ensemble average behave in the same way.

Nonequilibrium systems are not equally well understood. In particular, 'almost all' for steady-state NEMD models actually means 'almost none', since such steady states attribute probability 1 to sets of zero phase space volume. Dissipation amounts, in this case, to constraints that make typical certain vanishing subvolumes of $\mathcal{M}$. Indeed, exceedingly rare current fluctuation in equilibrium become the most likely currents in the steady state: 'counting' does not suffice.

The t-mixing condition may perhaps be used in this case. For any observable $\mathcal{O}$ and any integer n, let

$$E_n^{\mathcal{O},\delta} = \left\{ \Gamma : \overline{\mathcal{O}}(\Gamma) = \lim_{T\to\infty} \frac{1}{T}\int_0^T \mathcal{O}(S^t\Gamma)\,\mathrm{d}t \in [n\delta,(n+1)\delta) \right\} \qquad (47)$$

be the set of initial phases $\Gamma \in \mathcal{M}$ such that a measurement that lasts very many microscopic times yields a given value within a tolerance δ. These sets are disjoint,

$$E_n^{\mathcal{O},\delta} \cap E_{n'}^{\mathcal{O},\delta} = \emptyset, \quad \text{for } n \neq n'$$

and, because of the limit, they are invariant for the dynamics:

$$S^{-t}E_n^{\mathcal{O},\delta} = E_n^{\mathcal{O},\delta}$$

i.e. trajectories starting inside one of these sets remain inside forever; trajectories starting outside, never enter these sets. If the limit in Equation (47) exists for all Γ, the sets $E_n^{\mathcal{O},\delta}$ cover $\mathcal{M}$:

$$\bigcup_{n\in\mathbb{Z}} E_n^{\mathcal{O},\delta} = \mathcal{M}, \qquad \text{hence } \mu_0\left(\bigcup_{n\in\mathbb{Z}} E_n^{\mathcal{O},\delta}\right) = 1 \qquad (48)$$

This is a relatively delicate assumption: in general, given the dynamics S^t, it does not follow that $\overline{\mathcal{O}}(\Gamma)$ exists for *all* Γ. In general one can only prove that $\overline{\mathcal{O}}(\Gamma)$ exists for almost all Γ, meaning with the exception of a set of vanishing steady-state probability.[42] As mentioned above, this is not the desired situation, since almost all with respect to a steady-state distribution could mean a set of vanishing volume in $\mathcal{M}$. From the point of view of an experimentalist preparing the system in equilibrium, before subjecting it to dissipative forces, this is hardly acceptable.

Nevertheless, it is rather common in systems of physical interest that $\overline{\mathcal{O}}(\Gamma)$ exists for almost all Γ in the sense of phase space volumes. For instance, various attractors in $\mathcal{M}$, each characterised by a given time average, may together attract almost all trajectories.

Therefore, we assume that time averages exist with probability 1 with respect to μ_0. This assumption is weaker than ergodicity, since it does not require metric transitivity, or the uniqueness of the steady state. In particular, it is much more general than the mixing condition, that is often invoked to justify relaxation, in the sense of ensembles.

Let us now introduce the characteristic function χ_E of a set $E \subset \mathcal{M}$:

$$\chi_E(\Gamma) = \begin{cases} 1 \text{ if } \Gamma \in E \\ 0 \text{ if } \Gamma \notin E \end{cases}$$

Assuming that the characteristic functions $\chi_n^{\mathcal{O},\circ}$ of the sets $E_n^{\mathcal{O},\delta}$ verify t-mixing, we have:

$$\mu_0\left(E_n^{\mathcal{O},\delta}\right) - \mu_0\left(E_n^{\mathcal{O},\delta}\right)^2 = \mu_0\left(E_n^{\mathcal{O},\delta} \cap S^{-t}E_n^{\mathcal{O},\delta}\right) - \mu_0\left(S^{-t}E_n^{\mathcal{O},\delta}\right)\mu_0\left(E_n^{\mathcal{O},\delta}\right) \underset{t\to\infty}{\longrightarrow} 0$$

It follows that

$$\mu_0\left(E_n^{\mathcal{O},\delta}\right) = 0 \text{ or } 1,$$

where '= 1' holds for one and only one $n \in \mathbb{Z}$.

The t-mixing property for $\chi_n^{\mathcal{O},\delta}$ then appears to be sufficient but also necessary for single system relaxation, with a negligible set of exceptions. Indeed, if it holds, almost all (in the sense of phase space volumes) time averages take the same value, with an arbitrarily small error δ. In other words, under t-mixing, the counting argument for the irreversible relaxation to an equilibrium state, extends to dissipative dynamics. As for equilibrium we may state that not just the ensemble averages relax, but that they do so because all single systems relax to the same state.

5. Concluding remarks

- FRs are among the few exact relations for systems arbitrarily far from equilibrium. In particular, they are relevant for small systems, which cannot verify the conditions of local thermodynamic equilibrium. They are parameter free, hence they constitute a strong connection with the systems of interest. Transient (ensemble) FRs are very robust, since they require only reversibility. Moreover, they concern properties of the initial equilibrium state, that are revealed by nonequilibrium experiments. In this sense, they close the circle with the fluctuation dissipation relations, that obtain nonequilibrium properties from equilibrium experiments.

If a system does not tend to a steady state with fluctuations, the steady-state FRs obviously make no sense. Nevertheless the transient FRs, concerning the initial ensembles, hold at arbitrarily large times. Transient FRs differ substantially from steady-state FRs. Transient FRs are exact for all observation times τ; steady-state relations may only be approximately valid for finite τ, and require the system to be in steady state. Furthermore, from an experimental stand point, transient FRs correspond to sampling a large number of identical objects, or of repetitions of the same experiment, all starting in the same initial macrostate. Steady-state FRs may be verified on ensembles, but also following for a sufficiently long time a single object, in its steady- state evolution. Clearly, steady-state FRs have no relations with possible initial noninvariant states.

- Looking for a general formulation of transient FRs for the 'entropy production', led to the definition of the dissipation function:

$$\Omega^{(0)} = -G \cdot \partial_\Gamma \ln f^{(0)} - \Lambda$$

Its ubiquity in the theory presents $\Omega^{(0)}$ as a generalised thermodynamic potential, that is worth investigating of its own merits in statistical physics and in dynamical systems theory.

- The search for the minimal ingredients necessary for the steady-state FR led to the identification of the t-mixing condition [19]:

$$\lim_{t\to\infty}\left[\left\langle\left(\mathcal{O}\circ S^t\right)\mathcal{P}\right\rangle^{(0)} - \left\langle\mathcal{O}\circ S^t\right\rangle^{(0)}\langle\mathcal{P}\rangle^{(0)}\right] = 0$$

This decay of correlations with respect to μ_0, rather than an invariant probability distribution, constitutes a new notion in statistical physics, that is reminiscent of the linear response theory, but that leads to a response formula that is totally general:

$$\langle\mathcal{O}\rangle^{(t)} = \langle\mathcal{O}\rangle^{(0)} + \int_0^t \mathrm{d}s \left\langle\left(\mathcal{O}\circ S^s\right)\Omega^{(0)}\right\rangle^{(0)}$$

Ωt-mixing appears to be necessary and sufficient for ensemble relaxation to a steady state, and may be particularly useful in nonthermodynamic cases.

- The above ideas about a general theory of response have been here applied to the problem of irreversibility. In the case of convergence to an equilibrium state, the dynamics commonly trusted are the Hamiltonian ones. The result is a theory that explains irreversibility for systems of very many particles in terms of typicality, i.e. the fact that the microscopic phases corresponding to equilibrium macroscopic states are so overwhelmingly more 'numerous' than those corresponding to nonequilibrium states. This implies that a system starting in a nonequilibrium state whose dynamics explore the phase space without constraints, is bound both forward and backward in time to 'irreversibly' enter an equilibrium state. This argument is qualitatively convincing and rigorous in the case of ideal gases. To identify an arrow of time one must then consider the evolution of the whole universe, and postulate that it started from a very special initial condition.
- This argument appears however criticisable from numerous points of view. Moreover, it appears excessive if one only wants to investigate irreversibility within our daily experience. It may be more economical to refer to other kinds of models than the Hamiltonian ones. For instance those of NEMD have proved very effective in treating numerous aspects of real systems. The objection that they do not capture the profound nature of physical interactions, because harmed by fictitious forces can be equally turned against any other model of the physical world. Although this does not warrant success in dealing with the issue of irreversibility, it may be worthwhile to use these models to shed a different light on irreversibility.[10]

We have thus found that t-mixing for sets such as $E_o^{\mathcal{O},\delta}$ turns ensemble into single system relations. Then, assuming that time averages exist with μ_0-probability 1, i.e. for all initial $\Gamma \in \mathcal{M}$, apart from a set of zero volume, we have linked irreversibility to 'counting' even in the case of TRI dissipative systems, that had never been considered before, as far as we know. It remains to check more precisely the role of the large number of particles N, which is however implicit at least in the initial equilibrium ensemble f_0.

- Usually correlation functions are computed with respect to stationary distributions, that necessarily carry limited information about the evolution of macroscopic states. Differently, t-mixing represents the loss of memory of macrostates, hence it looks then better suited to deal with evolving systems, even in the absence of dissipation. The systems size N must play a role in this correlation decay with respect to the initial state, because anomalous FRs are associated with systems of few degrees of freedom.

Notes

1. For example, the model (1) corresponds to $G(\Gamma) = (\dot{\mathbf{q}}_i = \mathbf{p}_i/m + \mathbf{n}_x\gamma y_i, \dot{\mathbf{p}}_i = \mathbf{F}_i - \mathbf{n}_x\gamma p_{yi} - \alpha\mathbf{p}_i)$.
2. Thanks to TRI, $\overline{\alpha}_{i^*,\tau}$, the average of α over segment i^* equals $-\overline{\alpha}_{i,\tau}$, in agreement with (5).
3. One notable exception is afforded by gravitational wave detectors and similar experiments.[43,44]
4. The transient FR holds even in this situation, since it expresses the ratio between the initial probability of observing average negative values over a time τ, compared with the initial probability of observing positive values. For an even initial f_0, both probabilities are positive, although the first rapidly decreases with τ, due to the dissipative field. The transient FR quantifies precisely this process at all averaging times τ.
5. Consider all arrangements of $10^3 \times 10^3$ black and white pixels. The result is a dull movie: $\mathcal{M}$ contains 2^{10^6} pictures, among which the remotely regular ones constitute a very small fraction. The overwhelming majority are grey. If pictures are shown at a rate of 25 frames a second, and the movie goes through all of them before starting again, the period is $> 10^{301020}$ years! The fraction of time in which one does not see noisy arrangements is ridiculously small.

6. Note: usually this explanation of irreversibility is referred to the growth of the entropy of the universe, intended as a measure of disorder. Because entropy is however a questionable concept in the context of the violently nonequilibrium evolution of our universe, we merely refer to the 'numerosity' of states. For rarefied gases, these two notions come together in the definition of the Boltzmann entropy.
7. Actually, even the presence of extra additive constants of the motion would not make a difference: the reasoning can be repeated calling phase space the intersection of the corresponding hypersurfaces. Moreover, what matters is not the exploration of all phase space, which would take super-astronomical times even for systems with moderately large *N*, but the fact that the phase space regions corresponding to the range of the observables are visited. With this in mind, the reasoning can be continued in phase space, as usually, although imprecisely, done.
8. There are only several exceptions.[45,46]
9. After all, even the Hamiltonian description of atoms and molecules does not do that.[26]
10. Gauss expressed a similar view when he proposed his principle of least constraint: 'It is always interesting and instructive to regard the laws of nature from a new and advantageous point of view, so as to solve this or that problem more simply or to obtain a more precise presentation'.[47]

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Appendix 1. Ergodicity and mixing

The notion of ergodicity was originally developed to compute the macroscopic properties of physical systems from the dynamics of their microscopic constituents, by means of suitable averaging procedures. For instance, given Equation (2), in which the vector field G is determined by the forces acting on the system and by the particles' interactions, and given the observable $\mathcal{O}$, the associated macroscopic quantity is given by:

$$\overline{\mathcal{O}}(\Gamma) = \lim_{t\to\infty} \frac{1}{t} \int_0^t \mathcal{O}(S^s\Gamma)\mathrm{d}s. \tag{A1}$$

This reflects the fact that macroscopic observations occur on time scales which are long compared to the time scales of the microscopic dynamics, and that an observation amounts to a time average of the chosen observable $\mathcal{O}$. Equation A1 suffers from various difficulties of a practical nature, as previously discussed.[19] In any event, a system is called ergodic if

$$\overline{\mathcal{O}}(\Gamma) = \frac{1}{\mu(\mathcal{M})} \int_{\mathcal{M}} \mathcal{O}(y)\,\mathrm{d}\mu(y) = \langle \mathcal{O} \rangle_\mu \tag{A2}$$

for a properly chosen invariant probability measure μ on $\mathcal{M}$, for all observables $\mathcal{O}$, and for μ-almost all $\Gamma \in \mathcal{M}$.

One checks *a posteriori* whether assuming ergodicity is valid or not for the physical problem at hand, and one finds that the classical ensembles describe equilibrium situations very well, despite the fact that the mathematical notion of ergodicity is violated, for instance, by the ideal gas in a cubic box, by chains of harmonic oscillators, by blackbody radiation, etc. The fact is that the ergodic hypothesis can be adopted for *practical* purposes such as computing, in macroscopic equilibrium cases, the averages of a small set of physically relevant quantities. Nevertheless, the modern mathematical notion of ergodicity amounts to the following equivalent statements:

- (E1) for every integrable phase function Equation (A2) holds, except for a set of vanishing μ probability;
- (E2) except for a set of vanishing μ probability, $\tau_E(\Gamma) = \mu(E)$, where $E \subset \mathcal{M}$ is a μ-measurable set and

$$\tau_E(\Gamma) = \lim_{t\to\infty} \frac{1}{t} \int_0^t \chi_E\left(S^s\Gamma\right)\mathrm{d}s; \quad \text{with} \quad \chi_E\left(\Gamma\right) = \begin{cases} 1 & \text{if } \Gamma \in E \\ 0 & \text{else} \end{cases} \tag{A3}$$

  is the mean time in E;
- (E3) let $\mathcal{O}$ be integrable and let $\mathcal{O}(S^t\Gamma) = \mathcal{O}(\Gamma)$ for all t and all Γ. Then $\mathcal{O}(\Gamma) = C$ μ-almost everywhere, for a given $C \in \mathbb{R}$;
- (E4) the dynamical system $(S, \mathcal{M}, \mu)$ is *metrically indecomposable*, i.e. given the invariant set E, either $\mu(E) = 0$ or $\mu(E) = 1$.

We immediately notice that requiring $\mathcal{O}$ to be any integrable function, ergodicity is a very strong property, that is very hard to meet in systems of physical interest. But the physics of macroscopic systems needs much less; that's why the ergodic hypothesis is so successful.

The following statements are equivalent too:

- (M1) For every pair of measurable sets $D, E \subset \mathcal{M}$ one has:

$$\lim_{t\to\infty} \mu\left(S^{-t}D \cap E\right) = \mu(D)\mu(E) \tag{A4}$$

- (M2) for all $\mathcal{O}, \psi \in L_2(\mathcal{M}, \mu)$ the following holds:

$$\lim_{t\to\infty} \left\langle \left(\mathcal{O} \circ S^t\right) \psi \right\rangle_\mu = \langle \mathcal{O} \rangle_\mu \langle \psi \rangle_\mu \tag{A5}$$

We call *mixing* the dynamical systems that verify these two statements. Mixing is an even stronger property than ergodicity, in the sense that mixing systems are also ergodic, whereas not all ergodic systems are mixing. Property (M1) means that an initial probability distribution is spread all over the set of invariant probability 1. Property (M2) means that correlations within the steady state (i.e. microscopic correlations) decay in time.

Appendix 2. The dissipation function

The notion of dissipation is fundamental in nonequilibrium physics. Equilibrium processes are those taking place without dissipation; conversely, processes with dissipation are out of equilibrium.

From a microscopic viewpoint, the entropy of isolated systems represented by Hamiltonian dynamics and by the microcanonical ensemble equals the logarithm of the phase space volume of its state. In more general equilibrium cases, characterised by an ensemble f, Gibbs' formula holds:

$$S = -k_B \int \mathrm{d}\Gamma f(\Gamma) \ln f(\Gamma) \tag{B6}$$

and the dynamics preserves this equilibrium if it preserves f, rather than the phase space volumes. For this reason, we may call *dissipative with respect to an ensemble* those dynamics for which that ensemble is not invariant. It follows that Hamiltonian dynamics are not dissipative with respect to the microcanonical ensemble, because Hamiltonian dynamics preserve the microcanonical distribution, while the Gaussian IK dynamics are usually dissipative with respect to the microcanonical ensemble, because they do not preserve such an ensemble in general.

This notion of dissipation does not necessarily denote real energy dissipation; it is merely a useful mathematical concept, but it does acquire physical relevance under proper conditions. Indeed, let us recall the definition of the *Dissipation Function* Ω Equation (9):

$$\Omega(\Gamma) = -G(\Gamma) \cdot \frac{\mathrm{d}}{\mathrm{d}\Gamma} \ln f \bigg|_\Gamma - \Lambda(\Gamma) \tag{B7}$$

which is the difference between the actual changes in phase space volume and the changes associated with the ensemble, and let us consider equations of motion $\dot{\Gamma} = G(\Gamma)$ that are 'adiabatically incompressible', meaning that $\Lambda = 0$ for the associated adiabatic equations, i.e. the equations of motion excluding the thermostat.[11] Let us assume that the initial distribution of phases f may be generated by a single field-free ($F_e = 0$) thermostatted dynamics, hence it is preserved by the equilibrium dynamics.

For Gaussian isokinetic dynamics, with kinetic energy fixed at the value $K_0 = (dN - d - 1)k_BT = (dN - d - 1)/\beta$, we have:

$$\alpha(\Gamma) = -\frac{(\dot{H}_0(\Gamma) + \mathbf{J}(\Gamma) \cdot \mathbf{F}_\mathrm{e})\beta}{dN - d - 1}, \qquad \Lambda(\Gamma) = dN\alpha(\Gamma) + O_N(1) \tag{B8}$$

where adiabatic incompressibility is used to obtain the final equality, and $O_N(1)$ is a correction of order 1 in N parts. In this case, the equilibrium phase space distribution is expressed by

$$f_0(\Gamma) \sim e^{-\beta H_0}\delta(K(\Gamma) - K_0), \text{ hence } \frac{f_0(\Gamma)}{f_0(iS^\tau\Gamma)} = \exp\left\{\beta \int_0^\tau \dot{H}_0(\Gamma(s))\mathrm{d}s\right\}$$

This immediately implies that the time integral of Ω is proportional to the dissipative flux

$$\overline{\Omega}_{0,\tau}(\Gamma) = \beta \int_0^\tau \dot{H}_0(\Gamma(s))\mathrm{d}s + \overline{\Lambda}_{0,\tau}(\Gamma) = -\overline{(\mathbf{J} \cdot \mathbf{F}_\mathrm{e})}_{0,\tau} V\beta + O_N(1) \tag{B9}$$

apart from corrections that are negligible when N is large.

Analogously, for Nosé–Hoover dynamics, the equilibrium phase space distribution is the extended canonical distribution

$$f_0(\Gamma) \sim e^{-\beta(H_0+\frac{1}{2}Q\alpha^2)}, \text{ hence } \frac{f_0(\Gamma)}{f_0(iS^\tau\Gamma)} = \exp\left\{\beta\int_0^\tau (\dot{H}_0\Gamma(s) + Q\alpha\dot{\alpha})ds\right\}$$

and Equation (B7) leads again to the proportionality between Ω and the dissipative flux **J**. One may easily realise that the same holds in various other cases. Recently, the expression of the dissipation in terms of the phase space variation rate and of a total derivative has been considered by other authors, see e.g. Ref. [16, p.38], in which the microscopic definition of dissipation is associated with the possibility of defining in various fashions the phase space volumes.

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