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Approach to equilibrium in the Fokker-Planck equation for Hamiltonian systems

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Chapter 1

Introduction

The study of many-particles system has been the center of attention for many years in the history of physics. The fact that the precise observation of the exact motion of the single particle, in such systems, becomes out of our reach posed some non-trivial questions to be answered. How do we build a model of the system? Are the usual conservation laws of classical physics enough to describe its behaviour? The first steps in the direction of statistical mechanics still look obscure and cloudy to the new eye approaching the field; to discover the real premises at the base of the theory, it is necessary to dive quite deep in literature, and with an attentive attitude.

A rather famous example of how the blurry foundations of statistical mechanics can go unnoticed - and almost ignored - for many years is Boltzmann's *H-theorem*. Historically, its premises and how they brought to the theorem's thesis were widely criticized, and by many experts - Loschmidt and Zermelo being the main exponents of the criticism. Nonetheless, its experimental validity speaks for itself, as the consequences drawn from the theorem are still extensively in use. It appears, though, that the controversy has only faded out during time; the issue was never really resolved. In [1], Ageno brings a deep analysis of the Boltzmann-Loschmidt dispute, examining in detail where lied the unresolved misunderstanding between the two. At the heart of the H-theorem resides the conceptual gap one needs to overcome when going from classical deterministic mechanics to statistical mechanics; only it is not particularly obvious. Boltzmann's model of the ideal gas is composed of hard spheres performing elastic collisions with each other and with the walls - where the latter is considered so large that the result is only to reverse the momentum component of the particle that is normal to the wall. So, the foundation of Boltzmann's theorem is a completely deterministic system - and here lies the point of dispute -, so how can an irreversible process (H decreasing until equilibrium) be deduced, when the

system allows complete reversibility? In fact, the model proposed by Boltzmann is bound to always remember its initial conditions, and to depend solely on those. It is never possible to obtain a continuous set of possible momenta of the particles - i.e. to uniformly "cover" the phase space during evolution - since the collision only allow the momenta to "hop" from one value to another, all in a determined fashion, hence to endlessly add sets of measure zero to the phase space. Just like that, the thought of obtaining, in most cases, a Maxwell-Boltzmann distribution at equilibrium seems unrealistic. This feature is intrinsic of the model adopted, and no argument - be it deterministic or of a probabilistic nature - can make up for it unless some terrible sacrifices (like conserved momentum) are made (in detail, see [1]). The solution to the problem is to admit that the classical model introduced by Boltzmann is not a good model for the system, and that it does not accurately depict its underlying physics. To maintain the probabilistic characteristics of Boltzmann's discussion, one sees that, exactly, something *probabilistic* must be added to the model itself.

This is why the usual approach in studying the mathematical model of many-particles systems is to add a probabilistic component - hence to add a *stochastic force* - which takes into account all the random fluctuations that each particle can endure. But what is responsible for those random deviations? One could give countless explanations. Perhaps the most convincing is the one for which the wall of the box the system is enclosed in *cannot* produce an elastical collision with the particle. First of all, the wall is big with respect to the small particle, which is then able to "see" every flaw and every imperfection of the wall. The latter, then, will not be a straight wall for the particle, and therefore the dynamic of the collision earlier adopted will not be correct. Also, it is highly probable that the wall may not just let the particle collide, but might also, since made up of a lattice, capture the particle in some way and let it go - at some point - with an impredictable momentum. If we then imagine that the system is in contact, on the other side of the wall, with a thermal bath, one must also expect that the particle hitting the wall will also inherit some of the energy of the thermal bath, drastically increasing its velocity.

This is the kind of model we are going to adopt in our dissertation on equilibrium. As of the type of stochastic force to apply to the particles, we will add the stochastic component only on the momentum coordinates; this makes sense as we said above that the major changes the particles are subjected to are in energy (thermal agitation from the bath), not in position (see [5]). Since we do not have any reason to think that the random impulses are sent in a specific direction, we will consider their mean value to be zero; also, we will take into account that we are looking at uncorrelated collisions that last only for a very short time. If only the random force were to be added on the system, we would have that the kinetic energy of the particles

grows unboundedly with time; therefore, we must add a dissipative component which considers the viscous friction that the particles produce onto each other and prevents large amounts of kinetic energy. With these ingredients, we will derive the so called *Fokker-Planck equation*, which describes the time evolution of the probability density of systems with stochastic and dissipative factors. Our first objective, then, is to see how we can infer equilibrium (which will be described by the Gibbs' probability density) starting from the Fokker-Planck equation, and give an estimation of the characteristic time of equilibrium. All the considerations will be made regarding "classic" Hamiltonians (i.e. kinetic part + potential on position). Secondly, we intend to alter our model to make it a bit more realistic. As we said earlier, we imagine that the thermal agitation comes from the walls in contact with the thermal bath. Therefore, not all of the particles will be affected by it: only those in close proximity to the border. To mimic this effect, the stochastic noise mentioned before will be added only on the border of the system. One can see that such operation can be made only when dealing with solid objects - maybe liquids still - where the notion of *border* still bears some meaning. How does one define "border" on a gas? We might think to consider as affected by the thermal bath only the particles that enter within a thin region from the wall. But that would require us to actually know how many particles enter such region, and for how long - a request a bit too ambitious for our dissertation. For our purpose, we will not then treat gases; instead, we will focus our attention on solids and liquids, applying the stochastic-dissipative model for agitation only on a fixated, restricted subset of degrees of freedom, i.e. the momentum components of the particles at the outskirts.

Chapter 2

The Fokker-Planck equation

In this first chapter, we will go over a few basic concepts that make up the foundations for our discussion. First of all, we will need to define the mathematical properties of the stochastic process we are going to use, and then follow up - following the steps in [7] - with the derivation of the standard Fokker-Planck equation that comes from it. Once this is done, we will be able to discuss how to write the equation adhering to the Hamiltonian formalism.

2.1 Stochastic Methods

If we are to model the action of thermal bath on an object, we must forget the deterministic approach proposed by Hamilton's equations, since it will not take into account the thermal agitation the particles are subjected to. It is then necessary to define a process which allows us to mimic the randomness of the particles' motion, and to expand our concept of dynamic system to a probabilistic point of view - a *stochastic process*. What we are looking for is a continuous set of random variables; explicitly, we need a function

$$\xi: \ T \times \Omega \to \mathbb{R}^n : \ (t, \omega) \to \xi(t, \omega) \quad , \tag{2.1}$$

where $T = \mathbb{R}$ and $(\Omega, \sigma_\Omega, \mu)$ is the probability space we are working on - σ_Ω is a σ-algebra on Ω and μ is the probability density of the system. Generally, T is an interval of real numbers, as it usually indicates time. Then, for any fixed moment in time $\bar{t}$, any i-component of the process, $\xi_i(\bar{t}, \omega)$, is a random variable. Being such, observing multiple times the system at $\bar{t}$, one finds that ξ_i may take on different values; its expectation value is part of what characterizes the random variable, and consequently the stochastic process. Also, for any fixed $\bar{\omega} \in \Omega$, $\xi(t, \bar{\omega})$

is a n-dimentional function of time, and is called a 'sample function' of the process. To fully determine the particular stochastic process in use, one must not only specify what kind of random variable $\xi_i(\bar{t}, \omega)$ is; it is necessary to first specify the joint probability of those variables at different times. In other words, if we take a finite discrete set of instants $t_1 < t_2 < ... < t_N$, we find N vector functions $\xi^{(1)} = \xi(t_1, \omega)$, $\xi^{(2)} = \xi(t_2, \omega)$, ... , $\xi^{(N)} = \xi(t_N, \omega)$ with a joint probability distribution among them; to define the stochastic process, we must assign the joint probability distribution for any finite set of instants. For more on stochastic processes, see [5] and [4].

The stochastic process we will adopt in our model is called a "white noise" process, and it's one of the most used in the field of physics. Let us see its properties. First of all it is a Gaussian process of mean zero, so that the random vectors ξ satisfy, for any time $s \in \mathbb{R}_+$:

$$\langle \xi_i(s) \rangle = 0 \quad \forall i = 1, ..., n , \tag{2.2}$$

where the expectation value is done with respect to the distribution of $\xi_i(s)$. Also, the joint probability distribution of the process is described by

$$\langle \xi_i(s)\xi_j(s') \rangle = g_{ij}\delta(s - s') \quad \forall i, j = 1, ..., n \, ; \forall s, s' \in \mathbb{R}_+ , \tag{2.3}$$

where $\delta(s - s')$ is the Dirac delta function and g_{ij} is the i, j entry of the covariance matrix of the process (which must be constant and symmetric). This assures that the variables at different times are uncorrelated, so that any event which randomly happens at one time is completely independent of an event happening later, or earlier.

2.2   Origin of the Fokker-Planck equation

Once we add the stochastic component to the vectorial field describing the non-random part of the dynamic of the system (here called $u(t, x)$), we obtain the Langevin equation:

$$\dot{x} = u(t, x) + \xi(t) , \tag{2.4}$$

which can be written in the following way by integrating it on a small time interval (this form will be of greater use in afterward calculations):

$$\Delta x(t) = x(t + \Delta t) - x(t) = \int_t^{t+\Delta t} u(s, x(s))\mathrm{d}s + \int_t^{t+\Delta t} \xi(s)\mathrm{d}s . \tag{2.5}$$

If we group together the terms of higher order than the first of Δt (we will neglect them at a certain point), we find:

$$\int_t^{t+\Delta t} u(s, x(s))\mathrm{d}s = u(t, x(t))\Delta t + o(\Delta t) , \tag{2.6}$$

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and, defining the Wiener process $W(t) := \int_0^t \xi(s)\mathrm{d}s$,

$$\Delta W := W(t + \Delta t) - W(t) = \int_t^{t+\Delta t} \xi(s)\mathrm{d}s \quad . \tag{2.7}$$

It is quite easy to see that the properties of ξ imply that

$$\begin{aligned}
\langle \Delta W_i \rangle &= 0 \\
\langle \Delta W_i \Delta W_j \rangle &= g_{ij}\Delta t \quad .
\end{aligned} \tag{2.8}$$

Our goal is to obtain the equivalent of the continuity equation in the case of a vector field which bears a stochastic component. The general smooth density of a system described by such a vector field can be put in the following form:

$$\begin{aligned}
\rho(t, y) &:= \left\langle \int \delta(y - \Phi^t(x_0; \xi))\rho(0, x_0) \ \mathrm{d}V(x_0) \right\rangle_\xi = \\
&= \int \langle \delta(y - \Phi^t(x_0; \xi)) \rangle_\xi \rho(0, x_0) \ \mathrm{d}V(x_0) \quad , \tag{2.9}
\end{aligned}$$

where $\Phi^t(x_0; \xi)$ is the flow of the vector field. To lighten the notation, we will omit the pedice ξ on the mean value; we must remember that said mean is to be computed only on the stochastic component.

So, we can compute the evolution of the above density keeping in mind some of the properties seen above. Explicilty:

$$\begin{aligned}
\rho(t + \Delta t, y) - \rho(t, y) &= (*) = \left\langle \int [\delta(y - x(t + \Delta t)) - \delta(y - x(t))]\rho(0, x_0) \ \mathrm{d}V(x_0) \right\rangle = \\
&= \left\langle \int [\delta(x(t) + \Delta x(t) - y) - \delta(x(t) - y)]\rho(0, x_0)\mathrm{d}V(x_0) \right\rangle \tag{2.10}
\end{aligned}$$

Expanding the first δ at $x(t) - y$, we have

$$\begin{aligned}
(*) &= \left\langle \int \left[\sum_{i=1}^n \Delta x_i \frac{\partial}{\partial x_i} + \frac{1}{2}\sum_{i,j=1}^n \Delta x_i \Delta x_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} + \ldots \right] \delta(x(t) - y))\rho(0, x_0) \ \mathrm{d}V(x_0) \right\rangle = \\
&= -\sum_{i=1}^n \frac{\partial}{\partial y_i}\left\langle \int \Delta x_i \delta(x(t) - y)\rho(0, x_0)\mathrm{d}V(x_0) \right\rangle + \\
&+ \frac{1}{2}\sum_{i,j=1}^n \frac{\partial}{\partial y_i}\frac{\partial}{\partial y_j}\left\langle \int \Delta x_i \Delta x_j \delta(x(t) - y)\rho(0, x_0)\mathrm{d}V(x_0) \right\rangle + O(\langle \Delta x^3 \rangle) \quad , \tag{2.11}
\end{aligned}$$

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where $O(\langle \Delta x^3 \rangle) = o(\Delta t)$ because of the conditions on the stochastic term. Remembering (2.6) and (2.8) and taking in account that $\xi(s)$ is influential on Φ^t only for $s < t$, we move forward:

$$
\begin{aligned}
(1) \quad &:= \quad \left\langle \int \Delta x_i \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle = \\
&= \quad \left\langle \int [u_i(t, x(t)) \Delta t + o(\Delta t)] \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle + \\
&+ \quad \left\langle \int \left[\int_t^{t+\Delta t} \xi_i(s) \mathrm{ds} \right] \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle = \\
&= \quad u_i(t, y) \Delta t \left\langle \int \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle + o(\Delta t) + \\
&+ \quad \int \left\langle \int_t^{t+\Delta t} \xi_i(s) \mathrm{ds} \right\rangle \langle \delta(x(t) - y) \rangle \rho(0, x_0) \mathrm{dV}(x_0) = \\
&= \quad u_i(t, y) \rho(t, y) \Delta t + o(\Delta t) \quad ; \qquad\qquad\qquad\qquad (2.12)
\end{aligned}
$$

$$
\begin{aligned}
(2) \quad &:= \quad \left\langle \int \Delta x_i \Delta x_j \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle = \\
&= \quad \left\langle \int \left[\int_t^{t+\Delta t} \int_t^{t+\Delta t} \xi_i(s) \xi_j(s') \mathrm{ds}\mathrm{ds}' \right] \delta(x(t) - y) \rho(0, x_0) \mathrm{dV}(x_0) \right\rangle + o(\Delta t) = \\
&= \quad g_{ij} \rho(t, y) \Delta t + o(\Delta t) \quad . \qquad\qquad\qquad\qquad (2.13)
\end{aligned}
$$

Once we put all these terms together nicely, we finally find the Fokker-Planck equation:

$$
\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{n} \frac{\partial(\rho u)}{\partial y_i} + \frac{1}{2} \sum_{i,j=1}^{n} g_{ij} \frac{\partial^2(\rho)}{\partial y_i \partial y_j} \quad , \qquad\qquad (2.14)
$$

which can also be put in the form

$$
\frac{\partial \rho}{\partial t} = -\nabla_x \cdot (\rho u) + \frac{1}{2} \mathrm{Tr} \left[G \frac{\partial^2 \rho}{\partial y^2} \right] \quad . \qquad\qquad (2.15)
$$

2.3 The Fokker-Planck equation for Hamiltonian systems

We saw that the Fokker-Planck equation can be written in the form

$$
\frac{\partial \rho}{\partial t} = -\nabla_x \cdot (\rho X) + \frac{1}{2} \mathrm{Tr} \left[G \frac{\partial^2 \rho}{\partial x^2} \right] \quad , \qquad\qquad (2.16)
$$

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where x indicates the set of variables in the phase space Γ, X is the vector field describing our system, and G is the correlation matrix for the noise. We can find and equivalent form of said equation for the Hamiltonian case: we will use the Hamiltonian vector field X_H of the usual form, and add a dissipative component to the field depending on a parameter $\gamma > 0$. This is done in order to compensate the fact that the noise will have an average effect on our system, as it could increase its energy in a way that is inconsistent with a real physical system. Explicitly, for the field X we have

$$X = X_H - \gamma \begin{bmatrix} 0 \\ \nabla_p H \end{bmatrix} = \begin{bmatrix} \nabla_p H \\ -\nabla_q H \end{bmatrix} - \gamma \begin{bmatrix} 0 \\ \nabla_p H \end{bmatrix} \quad . \tag{2.17}$$

For the noise we choose to use white noise only present on the p-component; so we have that $\xi^{(q)} \equiv 0$, $\langle \xi_i^{(p)}(s) \rangle = 0$ and $\langle \xi_i^{(p)}(s) \xi_j^{(p)}(s') \rangle = 2D\delta_{ij}\delta(s - s')$. This means that the correlation matrix G appearing in the Fokker-Planck equation is in the form

$$G = \begin{bmatrix} \mathbb{0}_N & \mathbb{0}_N \\ \mathbb{0}_N & 2D\mathbb{1}_N \end{bmatrix} \quad . \tag{2.18}$$

Notice that

$$\begin{aligned} \nabla_x \cdot (\rho X) &= \{\rho, H\} - \gamma \nabla_p \rho \cdot \nabla_p H + \rho \nabla_x X_H - \gamma \rho \nabla_p \cdot \nabla_p H \\ &= \{\rho, H\} - \nabla_p \cdot (\gamma \rho \nabla_p H) \quad , \end{aligned} \tag{2.19}$$

while

$$\frac{1}{2} \operatorname{Tr} \left[G \frac{\partial^2 \rho}{\partial x^2} \right] = D\Delta_p \rho \quad . \tag{2.20}$$

So the expression for the Fokker-Planck equation in the Hamiltonian system is

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\} + \nabla_p \cdot (\gamma \rho \nabla_p H) + D\Delta_p \rho \quad . \tag{2.21}$$

Conditions on the parameters

Intuitively, the parameters that we used until now in our model (γ and D) cannot be independent on each other. To find a condition on said parameters, we look for an equilibrium solution of the Fokker-Planck equation, as a function of the Hamiltonian: $\rho_{eq} = f(H)$. When we insert this density into (2.21), we find that the partial derivative disappears as ρ is no more a function of time, along with the poisson parenthesis ($\{f(H), H\}$ always yields zero). We are left with:

$$\nabla_p \cdot [(\gamma f + Df') \nabla_p H] = (\gamma f' + Df'')|\nabla_p H|^2 + (\gamma f + Df')\Delta_p H = 0 \quad , \tag{2.22}$$

since $\nabla_p f(H) = f' \nabla_p H$. Notice that te equation is identically true if $g(H) := \gamma f + Df' = 0$; but, in this form, we cannot assert that this is the only way the equation can be satisfied, as the other parts of it are still functions of the Hamiltonian. If we assume that H has a smooth dependence on p, then H itself admits the following expansion:

$$H(q, p) = a(q) + b(q) \cdot p + \frac{1}{2} p \cdot Q(q) p + O(|p|^3) \quad . \tag{2.23}$$

With this assumption, equation (2.22) becomes

$$g'(H)\Big(|b|^2 + O(|p|)\Big) + g(H)\Big(\operatorname{Tr} Q + O(|p|)\Big) = 0 \quad . \tag{2.24}$$

The condition $g(H) = 0$ is obviously sufficient. If we take the limit for $p \to 0$ on the surface $S_E = \{(q, p) : H = E\}$ for a fixated energy level, we have

$$g'(E)|b|^2 + g(E) \operatorname{Tr} Q = 0 \quad , \tag{2.25}$$

which is generically not true since the coefficients in the Hamiltonian expansion are dependent on the energy level E. Thus, the condition $g(H) = 0$ is also necessary. If the equilibrium density is to satisfy such condition, it must be of the form:

$$\rho_{eq} = \frac{e^{-\frac{\gamma}{D} H}}{Z} \quad , \tag{2.26}$$

where Z is its partition function $\int_\Gamma e^{-\frac{\gamma}{D} H} dV$. Now, this means infinite solutions for γ and D independent of each other. But since we know that the thermostated system in equilibrium at temperature T only admits the Gibbs density

$$\rho_{Gibbs} = \frac{e^{-\frac{1}{T} H}}{Z_{Gibbs}} \quad , \tag{2.27}$$

it follows that the parameters must satisfy the relation

$$\frac{D}{\gamma} = T \quad , \tag{2.28}$$

which is often called the "Einstein relation".

Chapter 3

Useful inequalities

In this chapter we are going to state (and demonstrate in one case) a couple of inequalities; both of them will prove to be useful in later calculations (Villani also uses them in [6] and [3]). In particular, the first inequality - the Poincarè for Gaussian measures - will have applications in our study of mechanical systems. In fact, since the kinetic component of the Hamiltonian of that case is of the form $\sum_i \frac{p_i^2}{2m}$, the Gibbs probability density $\rho = e^{-\beta H}$ shows a Gaussian factor. The other inequality - the so called "Brascamp-Lieb inequality" - can give more general results, as it deals with exponential measures of the form $e^{-V(x)}\mathrm{d}x$, with $V(x)$ being a convex function. It will be useful in understanding which types of non-mechanical system can be studied with our model, and where may complications lie in doing so.

3.1 Poincarè inequality for gaussian measures

We now wish to demonstrate that a Poincarè inequality still holds in the case of a gaussian measure $\mathrm{d}\mu = \frac{1}{\sqrt{2\pi}}e^{-\frac{x^2}{2}}\mathrm{d}x$. The proof was inspired by [2] and mostly [8]. Naming $L_2(\mu)$ the space of square-integrable functions on our measure $\mathrm{d}\mu$, we will demonstrate the following:

$$\|\nabla f\|_{L_2(\mu)}^2 = \int |\nabla f|^2 \ \mathrm{d}\mu \geq C \operatorname{Var}_\mu(f) = C\left[\int f^2 \ \mathrm{d}\mu - \left(\int f \ \mathrm{d}\mu\right)^2\right] \ , \quad (3.1)$$

where C is the general constant that appears in Poincarè-like inequalities. In this case we will find that $C = 1$.

3.1.1 Hermite Polynomials

The key to this proof are the Hermite polynomials: we know that the eigenfunctions of the one-dimentional quantum harmonic oscillator form a basis on $L_2(\mathbb{R})$ (with the usual scalar product). These eigenfunctions are constructed using specifically the Hermite polynomials:

$$\phi_n(x) = c(\alpha)\frac{1}{\sqrt{n!}}e^{-\frac{\alpha^2 x^2}{4}}H_n^p(\alpha x) \quad , \tag{3.2}$$

where c is a constant depending on the parameter α and $H_n^p(\xi)$ are the "probabilistic" Hermite polynomials, given by

$$H_n^p(x) = \left(-1\right)^n e^{x^2/2}\frac{d^n}{dx^n}e^{-x^2/2} \quad . \tag{3.3}$$

As one can quickly see, these polynomials are suited to be a basis in $L_2(\mu)$:

$$\langle \phi_n | \phi_m \rangle = const. \int H_n^p(x)H_m^p(x)e^{\frac{-x^2}{2}} \, \mathrm{dx} = const. \int H_n^p(x)H_m^p(x) \, \mathrm{d}\mu = \delta_{n,m} \quad . \tag{3.4}$$

To simplify the notation in our proof we will not consider the normalization constant as it will not play a significant role in our calculations, but to do this we need to redefine our Hermite polynomials, in order to proceed correctly. Explicitly, we will use $H_n(x) := \frac{1}{\sqrt{n!}}H_n^p(x)$ as our basis in $L_2(\mu)$.

3.1.2 Proof

Let us introduce the operator

$$\mathrm{L}\, f(x) := -f''(x) + xf'(x) \quad . \tag{3.5}$$

Using Hermite's differential equation for probabilistic Hermite polynomials (which still holds for our custom defined polynomials)

$$H_n''(x) - xH_n'(x) + nH_n(x) = 0 \quad , \tag{3.6}$$

we can see that the polynomials are exactly the eigenfunctions of the operator L:

$$\mathrm{L}\, H_n(x) = nH_n(x) \quad . \tag{3.7}$$

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Let us first see that this operator is symmetric, meaning that $L = L^\dagger$. Knowing that any function $f, g \in L_2(\mu)$ can be written as a linear combination of Hermite polynomials, we have

$$\langle L\,f | g \rangle \;\; = \sum_{n,m} \alpha_n \beta_m \langle L\,H_n | H_m \rangle = \sum_n n \alpha_n \beta_n \tag{3.8}$$

$$\langle f | L\,g \rangle \;\; = \sum_{n,m} \alpha_n \beta_m \langle H_n | L\,H_m \rangle = \sum_m m \alpha_m \beta_m \quad . \tag{3.9}$$

The operator is also self-adjoint in $L_2(\mu)$; to see how, let us indicate the Hamiltonian operator of the harmonic oscillator with

$$\mathcal{H} = -\frac{\partial^2}{\partial x^2} + \alpha^2 x^2 + K \quad , \tag{3.10}$$

where α is the appropriate constant for the harmonic oscillator and K is just a shift in energy (remember that the energy of the system is defined up to a constant). We know that $\mathcal{H}$ is self-adjoint in $L_2(\mathbb{R})$, so that for $\eta \in L_2(\mathbb{R})$, $\exists\, \chi \in L_2(\mathbb{R})$ such that $\forall \psi \in L_2(\mathbb{R})$, $\langle \eta | \mathcal{H}\psi \rangle = \langle \chi | \psi \rangle$. If we define a new measure $\mathrm{d}\mu' = \rho'^2 \mathrm{d}x$, where $\rho' = Ae^{-\frac{\alpha x^2}{2}}$, we have that $f \in L_2(\mu)$ implies $f \in L_2(\mu')$, as the two measures only differ on constants which will not affect the scalar product if not, precisely, for a constant. Then, if we take $\psi = \rho' f$ we automatically have that $\psi \in L_2(\mathbb{R})$, and, choosing the appropriate value for K,

$$
\begin{aligned}
\mathcal{H}(\psi) \;\; &= \;\; \mathcal{H}(\rho' f) = -\frac{\partial^2}{\partial x^2}(\rho' f) + \alpha^2 x^2 \rho' f + K \rho' f = \\
&= \;\; -\rho' f \alpha^2 x^2 - \alpha \rho' f - \rho' \frac{\partial^2 f}{\partial x^2} + \rho' x \frac{\partial f}{\partial x} + \alpha^2 x^2 \rho' f + K \rho' f = \\
&= \;\; -\rho' \frac{\partial^2 f}{\partial x^2} + \rho' x \frac{\partial f}{\partial x} = \rho'\,L(f) \quad .
\end{aligned}
\tag{3.11}
$$

Then, for what we said before about the self-adjointness of $\mathcal{H}$, we can take $\psi = \rho' f$, $\eta = \rho' \eta'$, $\chi = \rho' \chi'$ (with $f, \eta', \chi' \in L_2(\mu')$), and shift the condition using the scalar product on $L_2(\mu')$. So we have that, for $\eta' \in L_2(\mu')$, $\exists\, \chi' \in L_2(\mu')$ such that $\forall f \in L_2(\mu')$, $\langle \eta' | Lf \rangle_{\mu'} = \langle \chi' | f \rangle_{\mu'}$. This proves that the operator L is self-adjoint in $L_2(\mu)$.

Using (3.8) it is easy to see that $\langle L\,f | f \rangle = \sum_n n \alpha_n^2$. Also, for the probabilistic Hermite polynomials it holds that $H_n^{p\,\prime}(x) = n H_n^p(x)$, which implies the following:

$$H_n'(x) = \sqrt{n} H_n(x) \quad ; \tag{3.12}$$

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it is now obvious that $\langle f'|f' \rangle = \sum_n n\alpha_n^2$, thus

$$\langle \mathrm{L}\, f|f \rangle = \|f'\|^2 \quad . \tag{3.13}$$

Before we proceed, we need to consider another operator:

$$\Pi f := f - \int f \mathrm{d}\mu \quad . \tag{3.14}$$

Notice that the only polynomial $H_n(x) \in ker(\mathrm{L})$ is $H_0(x)$, which is a constant; it follows that $\Pi H_0(x) = 0$. It also means that if $H_n(x) \notin ker(\mathrm{L})$, then $\int H_n(x) \, \mathrm{d}\mu = 0$ as a consequence of the orthogonality of the basis. Therefore:

$$\Pi H_n(x) = H_n(x) \quad \forall n \neq 0 \quad . \tag{3.15}$$

We are now ready to compute the variance of a general function $f \in L_2(\mu)$:

$$
\begin{aligned}
\langle \Pi f|f \rangle = \mathrm{Var}_\mu(f) \;\; &= \;\; \sum_{n,m} \alpha_n \alpha_m \big\langle \Pi H_n(x) \big| H_m(x) \big\rangle \\
&= \;\; \sum_{n,n \neq 0} \sum_m \alpha_n \alpha_m \big\langle H_n(x) \big| H_m(x) \big\rangle \\
&= \;\; \sum_{n,n \neq 0} \alpha_n^2 \quad ; \tag{3.16}
\end{aligned}
$$

while the square norm of its first derivative is

$$\langle \mathrm{L}\, f|f \rangle = \|f'\|^2 = \sum_n n\alpha_n^2 = \sum_{n,n \neq 0} n\alpha_n^2 \geq \sum_{n,n \neq 0} \alpha_n^2 \quad . \tag{3.17}$$

We just proved that $\langle \mathrm{L}\, f|f \rangle \geq \langle \Pi f|f \rangle$, so the Poincarè inequality is indeed valid in our case of a gaussian measure, with the constant C set to 1.

3.2   Brascamp-Lieb inequality

The Brascamp-Lieb inequality, which we will not demonstrate here (see the idea of the proof in [8]), generalizes the Poincarè inequality, as it is applicable to any measure of the type

$$\mathrm{d}\mu = e^{-V(x)} \mathrm{d}x \quad , \tag{3.18}$$

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as long as the function $V(x)$ is convex, i.e. $V'' := \text{Hess}(V)$ is a positive definite matrix. It reads:

$$\text{Var}(f) \leq \int [(V'')^{-1} \nabla f] \cdot \nabla f \, d\mu \quad . \tag{3.19}$$

We won't be using exactly this equation: under certain conditions, the Brascamp-Lieb inequality can be put in the form of a Poincarè inequality, which we will find more suited for our needs.

3.2.1 From Brascamp-Lieb to Poincarè

Let us suppose that for our potential $V(x)$ it exists a positive constant, λ, for which $V(x) - \lambda|x|^2$ is a convex function. This means that the matrix

$$M(x) := V''(x) - 2\lambda \mathbb{1} \tag{3.20}$$

is positive definite. Then, all of its eigenvalues - let us indicate them with the letter m - must be positive. Notice that

$$Mu_i = (V'' - 2\lambda\mathbb{1})u_i = m_i u_i \quad \Leftrightarrow \quad V''u_i = (m + 2\lambda)u_i = \theta_i u_i \quad , \tag{3.21}$$

where u_i are the eigenvectors of both M and V'' and θ_i are the eigenvalues of V''. Then, since $m_i \geq 0 \ \forall i$, it must be that

$$\theta_i = m_i + 2\lambda \geq 2\lambda \ , \quad \forall i. \tag{3.22}$$

Thanks to the spectral decomposition theorem, one can define the projectors of V'' as $P_i = u_i u_i^T$ and write the matrix as:

$$V'' = \sum_i \theta_i P_i \quad . \tag{3.23}$$

The same can be said for its inverse matrix, knowing that its eigenvectors are the same, and that the eigenvalues are the reciprocal of the original ones. Therefore:

$$(V'')^{-1} = \sum_i \frac{1}{\theta_i} P_i \quad , \tag{3.24}$$

where, because of condition (3.22), we have

$$\frac{1}{\theta_i} \leq \frac{1}{2\lambda} \ , \quad \forall i. \tag{3.25}$$

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Now we have all the instruments to analyze the scalar product found in the Brascamp-Lieb inequality:

$$
\begin{aligned}
\nabla f \cdot (V'')^{-1} \nabla f &= \sum_i \frac{1}{\theta_i} \nabla f \cdot P_i \nabla f = \sum_i \frac{1}{\theta_i} \nabla f \cdot u_i u_i^T \nabla f = \\
&= \sum_i \frac{1}{\theta_i} (u_i \cdot \nabla f)^2 \le \frac{1}{2\lambda} \sum_i (u_i \cdot \nabla f)^2 = \\
&= \frac{1}{2\lambda} \nabla f \cdot \sum_i P_i \nabla f = \frac{1}{2\lambda} |\nabla f|^2 \quad,
\end{aligned}
\tag{3.26}
$$

where in the last step we used the property of projectors for which $\sum_i P_i = \mathbb{1}$.

Finally, with the existence of such λ as the only condition, we proved that the Brascamp-Lieb inequality leads to a Poincarè-like inequality:

$$
\text{Var}(f) \le \frac{1}{2\lambda} \int |\nabla f|^2 \mathrm{d}\mu \quad.
\tag{3.27}
$$

Chapter 4

Approach to equilibrium for mechanical systems

In this part of our dissertation we would like to focus mainly on Hamiltonian mechanical system, i.e. those system in which the Hamiltonian reads

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) \quad, \tag{4.1}$$

where with the notation (q) we wish to indicate the generic dependence of the potential V on the set of variables $\{q_1, q_2, ..., q_N\}$. For now, we will always consider physical system in contact with a thermal bath; to model the behaviour of the system, we insert a stochastic component, followed by some dissipation, on each particle of the object/material, i.e. on every degree of freedom. The noise/dissipation pair used in this model is the same we used to evaluate the Fokker-Planck equation in Hamiltonian systems in section 2.3. Our goal is to study said systems and their approach to equilibrium. In particular, we want to prove that such a system which is not in a situation of equilibrium will eventually reach the well known equilibrium for a canonical ensemble. To do so, we will study the deviation from equilibrium and its variation through time, with a close look at its norm. In addition, we are also going to contemplate the evolution of the free energy of the system, to see if our methods are consistent with known principles of thermodynamics and statistical mechanics.

4.1 Evolution of deviation in Gibbs norm

Using the Fokker-Planck equation in the Hamiltonian case, in this section we are going to analyze what happens to the norm of the equilibrium density deviation.

We are working under the thermodynamic limit, in which the number of particles N is considered to be very big; in our dissertation we will have it approach infinity. Because of this it is crucial to predetermine which norm we want to work with, as different norms operating on infinite-dimentional spaces lead to different results. The wisest choice is the one with a specific physical meaning, in a way that we will trust our results to be physically consistent. We will see that the norm of said deviation gradually reduces as time passes, until equilibrium is reached. We will also be able to give an estimation of the characteristic time of approach to equilibrium.

4.1.1   Evolution of density

The Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\} + \nabla_p \cdot (\gamma \rho \nabla_p H) + D \Delta_p \rho \tag{4.2}$$

describes the change in time of the out-of-equilibrium probability density

$$\rho = \rho_{eq} + \delta\rho = \rho_{eq}(1 + \eta) \ , \tag{4.3}$$

where ρ_{eq} is the Gibbs density $Ce^{-\frac{1}{T}H}$. Since ρ_{eq} is already normalized, and ρ also must be, it follows that $\int \eta \rho_{eq} \, dV = 0$. Thus, if we define a measure $d\mu_{eq} = \rho_{eq}dV$, we shall have that

$$\int \eta \, d\mu_{eq} = 0 \ . \tag{4.4}$$

When we insert the given expression for ρ in (4.2), we find:

$$\rho_{eq}\frac{\partial \eta}{\partial t} = -\{\rho_{eq}\eta, H\} + \nabla_p \cdot (\gamma \rho_{eq}\eta \nabla_p H) + D \Delta_p (\rho_{eq}\eta) \ . \tag{4.5}$$

Let us study its addends:

$$\alpha \; := \; \nabla_p \cdot (\gamma \rho_{eq}\eta \nabla_p H) = \gamma \rho_{eq}\eta \Delta_p H + \gamma \eta \left(-\frac{1}{T} \right) |\nabla_p H|^2 \rho_{eq} + \gamma \rho_{eq} \nabla_p \eta \cdot \nabla_p H \tag{4.6}$$

$$\beta \; := \; D \Delta_p (\rho_{eq}\eta) = D \nabla_p \cdot \left(-\frac{1}{T} \nabla_p H \rho_{eq}\eta + \rho_{eq} \nabla_p \eta \right) =$$

$$= \; D \left[-\frac{1}{T} \Delta_p H \rho_{eq}\eta + \frac{1}{T^2} |\nabla_p H|^2 \rho_{eq}\eta - \frac{2}{T} \rho_{eq} \nabla_p H \cdot \nabla_p \eta + \rho_{eq} \Delta_p \eta \right] \ . \tag{4.7}$$

Then we have

$$\alpha + \beta = -\gamma \rho_{eq} \nabla_p H \cdot \nabla_p \eta + \gamma T \rho_{eq} \Delta_p \eta \ , \tag{4.8}$$

which gives

$$\rho_{eq}\frac{\partial \eta}{\partial t} = -\rho_{eq}\{\eta, H\} - \gamma\rho_{eq}\nabla_p H \cdot \nabla_p \eta + \gamma T \rho_{eq}\Delta_p \eta \quad . \tag{4.9}$$

4.1.2 Evolution of the norm

We are interested in studying the temporal evolution of the quantity η, which bears the physical meaning of the deviation from equilibrium; in particular, we would like to show that said quantity will eventually approach zero, and give an estimation of its characteristic time. To do this we shall look closely at the evolution of the norm of η: due to the fact that we are interested in physically meaningful results, the best choice for the measure in which to calculate the norm is precisely the previously defined Gibbs measure $d\mu_{eq}$. Using equation (4.9), we have

$$\begin{aligned} \frac{d}{dt}\int \frac{\eta^2}{2}\,d\mu_{eq} &= \int \eta\frac{\partial \eta}{\partial t}\,d\mu_{eq} = -\int \rho_{eq}\{\eta^2/2, H\}\,dV + \\ &\quad -\gamma\int \rho_{eq}\nabla_p H \cdot \nabla_p(\eta^2/2)\,dV + \gamma T\int \rho_{eq}\eta\Delta_p\eta\,dV = \\ &= \gamma T\int \nabla_p\rho_{eq}\cdot \nabla_p(\eta^2/2)\,dV + \gamma T\int \eta\Delta_p\eta\,d\mu_{eq} \quad, \end{aligned} \tag{4.10}$$

where the Poisson brackets disappear, since

$$\begin{aligned} \int \rho_{eq}\{\eta^2/2, H\}\,dV &= \int \rho_{eq}\nabla(\eta^2/2)\cdot J\nabla H dV = \int \nabla\cdot[(\eta^2/2)\rho_{eq}J\nabla H]dV - \\ &\quad -\int (\eta^2/2)\rho_{eq}\nabla\cdot J\nabla H dV - \int (\eta^2/2)\nabla\rho_{eq}\cdot J\nabla H dV = \\ &= \frac{1}{T}\int (\eta^2/2)\rho_{eq}\nabla H \cdot (J\nabla H)dV = 0 \quad; \end{aligned} \tag{4.11}$$

where it was used the fact that η vanishes at infinity in using the divergence theorem, and that $\nabla H \cdot J\nabla H = \nabla\cdot J\nabla H = 0$. Back to our equation; performing an integration by parts, and making use of the divergence theorem, we proceed this way:

$$\begin{aligned} \frac{d}{dt}\int \frac{\eta^2}{2}\,d\mu_{eq} &= \gamma T\int \nabla_p\cdot\left(\rho_{eq}\nabla_p(\eta^2/2)\right)\,dV + \\ &\quad -\gamma T\int \rho_{eq}\Delta_p(\eta^2/2)\,dV + \gamma T\int \eta\Delta\eta\,d\mu_{eq} = \\ &= \gamma T\int \left(\eta\Delta_p\eta - \Delta_p(\eta^2/2)\right)\,d\mu_{eq} \quad . \end{aligned} \tag{4.12}$$

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With the following calculation,

$$\Delta_p(\eta^2/2) = \nabla_p \cdot (\eta \nabla_p \eta) + |\nabla_p \eta|^2 + \eta \Delta_p \eta \quad , \tag{4.13}$$

we finally find that

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \frac{\eta^2}{2} \, \mathrm{d}\mu_{\mathrm{eq}} = -\gamma T \int |\nabla_p \eta|^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad . \tag{4.14}$$

4.1.3   Use of the Poincarè inequality

Since we are considering the physical case of N particles in which the Hamiltonian is of the form

$$H(q, p) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q) \quad , \tag{4.15}$$

the Gibbs measure reads:

$$\mathrm{d}\mu_{\mathrm{eq}} = A e^{-\frac{1}{T} V(x)} \prod_i B_i e^{-\frac{1}{T} \frac{p_i^2}{2m_i}} \, \mathrm{d}V \quad , \tag{4.16}$$

so that the integral in the second term of equation (4.14) can split in a sum of N integrals of this type:

$$\int \left(\int \left(\frac{\partial \eta}{\partial p_i} \right)^2 B_i e^{-\frac{1}{T} \frac{p_i^2}{2m_i}} \, \mathrm{d}p_i \right) \mathrm{d}\tilde{\mu}_{\mathrm{eq}} \quad ; \tag{4.17}$$

where $\mathrm{d}\tilde{\mu}_{\mathrm{eq}}$ is what remains of the Gibbs measure after we isolate one of its factors. One can see that the inner integral is a good candidate for which to use the Poincarè inequality we previously proved for gaussian measures. Notice that the function η has zero mean, so its variance equals its square norm. If we operate on the variables, we obtain the following inequality:

$$\int \left(\frac{\partial \eta}{\partial p_i} \right)^2 B_i e^{-\frac{1}{T} \frac{p_i^2}{2m_i}} \, \mathrm{d}p_i \geq \frac{1}{Tm_i} \int \eta^2 \, B_i e^{-\frac{1}{T} \frac{p_i^2}{2m_i}} \, \mathrm{d}p_i \quad ; \tag{4.18}$$

once we apply it to (4.17) we can reassemble the original measure, obtaining

$$\int \left(\frac{\partial \eta}{\partial p_i} \right)^2 \mathrm{d}\mu_{\mathrm{eq}} \geq \frac{1}{Tm_i} \int \eta^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad . \tag{4.19}$$

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Adding up all the integrals we find an inequality for (4.14):

$$-\gamma T \int (\nabla_p \eta)^2 \, \mathrm{d}\mu_{\text{eq}} \leq -\gamma \Big(\sum_{i=1}^{N} \frac{1}{m_i} \Big) \int \eta^2 \, \mathrm{d}\mu_{\text{eq}} \quad , \tag{4.20}$$

which implies a differential inequality for the square norm of η:

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \eta^2 \, \mathrm{d}\mu_{\text{eq}} \leq -2\gamma \Big(\sum_{i=1}^{N} \frac{1}{m_i} \Big) \int \eta^2 \, \mathrm{d}\mu_{\text{eq}} \quad . \tag{4.21}$$

The solution for (4.21) is clearly:

$$\int \eta^2 \, \mathrm{d}\mu\text{eq} \leq A e^{-2\gamma \left(\sum_{i=1}^{N} \frac{1}{m_i} \right) \cdot t} \quad , \tag{4.22}$$

which, in the case of particles of same mass m, becomes

$$\int \eta^2 \, \mathrm{d}\mu\text{eq} \leq A e^{-\frac{2\gamma N}{m} \cdot t} \quad . \tag{4.23}$$

4.1.4   Characteristic time of equilibrium

Thanks to this result we are able to give a (superior) estimation of the characteristic time of $\|\eta\|^2$, which means that we can estimate the average time in which our system will reach equilibrium. From (4.23) we can say that the characteristic time of the approach to equilibrium depends on the mass and number of particles, and on the stochastic parameter γ. Precisely:

$$\tau_{eq} \leq \frac{m}{2\gamma N} \quad , \tag{4.24}$$

or, in the case of different masses,

$$\tau_{eq} \leq \frac{1}{2\gamma \sum_{i=1}^{N} \frac{1}{m_i}} \quad . \tag{4.25}$$

Limits for γ

In our dissertation we decided to mimic the effect of the thermal bath on the particles adding fictitious stochastic forces and a dissipative term to balance. Unfortunately, this is still an approximation; if we decide to apply this method to a system in which the contribution of thermal agitation is prevalent on other effects, then our results will present too much of an uncertainty. We would like, then, to restrict to cases in which the stochastic component is very small, in a way to be confident with our result. In other words, we want to see what happens to our thermostated system when the stochastic parameter γ tends to zero.

If we only impose that $\gamma \to 0$, then we would have that

$$\tau_{eq} \leq \frac{m}{2\gamma N} \to \infty \quad , \tag{4.26}$$

which bears no significance. One way we can make γ approach zero is to anchor its value to the number of particles N, and make the latter approach infinity. Specifically, we would want

$$\gamma \propto \frac{1}{N} \quad ; \tag{4.27}$$

just so that our superior limit to the time τ_{eq} is still finite, while γ is small.

4.2   Evolution of Free Energy

We have seen that the probability density describing the system approaches in time Gibbs' probability measure, which describes the system in a state of equilibrium. What we now wish to check is if this approach is consistent with the physical theory. In thermodynamics, fundamental physical quantities used to describe a system are internal energy, free energy and entropy. The first one is obtained finding the mean value of the Hamiltonian, using the probability density of the system:

$$U(\rho) = \langle H \rangle_\rho = \int_\Gamma H\rho\,\mathrm{dV} \quad , \tag{4.28}$$

while the entropy can be written as

$$S(\rho) = -\int_\Gamma \rho \log \rho\,\mathrm{dV} \quad . \tag{4.29}$$

From these two quantities one can define the free energy:

$$F(\rho) = U(\rho) - TS(\rho) = \int_\Gamma (H\rho + T\rho \log \rho)\mathrm{dV} \quad . \tag{4.30}$$

The free energy F is supposed to be at minimum when the system reaches equilibrium. Let us see if this holds true, by computing the time derivative of F and studying its evolution in a similar fashion to the previous section, where we studied the norm of the deviation.

4.2.1   Time derivative

Using the Fokker-Planck equation as the evolution of ρ, one can compute the time derivative of the free energy as follows:

$$
\begin{aligned}
\frac{\mathrm{d}F}{\mathrm{dt}} &= \int (H + T \log \rho) \frac{\partial \rho}{\partial t} \mathrm{dV} + T \int \frac{\partial \rho}{\partial t} \mathrm{dV} = \\
&= \int (H + T \log \rho)[-\{\rho, H\} + \nabla_p \cdot (\gamma \rho \nabla_p H) + D \Delta_p \rho] \mathrm{dV} \qquad (4.31)
\end{aligned}
$$

During the next steps, one should remember that we are working with a probability density which, along with its gradient, vanishes sufficiently fast at infinity in the Γ space, so that, when possible, one can use the divergence theorem in the following way:

$$
\int_\Gamma \nabla \cdot (\rho \vec{v}) \mathrm{dV} = \int_{\partial \Gamma} (\rho \vec{v}) \cdot \mathrm{d}\vec{\Sigma} = 0 \quad ; \qquad (4.32)
$$

this applies also when the vector to which we calculate the divergence of is proportional to the gradient of ρ. Moreover, the same concept can be applied if the divergence is restricted to the (p) components. Keeping this in mind, along with the fact that $\nabla \cdot (J \nabla f) = 0$, the terms of equation (4.31) can be easily calculated in the following manner:

$$
\begin{aligned}
A \quad &:= \quad -\int (H + T \log \rho) \{\rho, H\} \mathrm{dV} \\
&= \quad -\int H \nabla \rho \cdot J \nabla H \mathrm{dV} - \int T \log \rho \nabla \rho \cdot J \nabla H \mathrm{dV} = \\
&= \quad -\frac{1}{2} \int \nabla \rho \cdot J \nabla (H^2) \mathrm{dV} - \int T \nabla (\rho \log \rho - \rho) \cdot J \nabla H \mathrm{dV} = \\
&= \quad -\frac{1}{2} \int \nabla \cdot [\rho J \nabla (H^2)] \mathrm{dV} - \int T \nabla \cdot [(\rho \log \rho - \rho) J \nabla H] \mathrm{dV} = \\
&= \quad 0 \quad ; \qquad (4.33)
\end{aligned}
$$

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$$
\begin{aligned}
B \quad &:= \quad \int [T \log \rho \nabla_p \cdot (\gamma \rho \nabla_p H) + DH \Delta_p \rho] \mathrm{dV} \\
&= \quad \int \gamma T \nabla_p \cdot (\rho \log \rho \nabla_p H) \mathrm{dV} - \int \gamma T \nabla_p H \cdot \nabla_p \rho \mathrm{dV} + \\
&+ \quad \int D \nabla_p \cdot (H \nabla_p \rho) \mathrm{dV} - \int D \nabla_p H \cdot \nabla_p \rho \mathrm{dV} = \\
&= \quad -2\gamma T \int \nabla_p h \cdot \nabla_p \rho \mathrm{dV} \quad ;
\end{aligned}
\tag{4.34}
$$

$$
\begin{aligned}
C \quad &:= \quad \int [H \nabla_p \cdot (\gamma \rho \nabla_p H) + DT \log \rho \Delta_p \rho] \mathrm{dV} = \\
&= \quad \int \gamma \nabla_p \cdot (\rho H \nabla_p H) \mathrm{dV} - \int \gamma \rho |\nabla_p H|^2 \mathrm{dV} + \\
&+ \quad \int DT \nabla_p \cdot (\log \rho \nabla_p \rho) \mathrm{dV} - \int DT \frac{|\nabla_p \rho|^2}{\rho} \mathrm{dV} = \\
&= \quad -\gamma \int [|\nabla_p H|^2 + T^2 |\nabla_p \log \rho|^2] \rho \mathrm{dV} \quad .
\end{aligned}
\tag{4.35}
$$

So, adding each term, we finally have:

$$
\frac{\mathrm{d}F}{\mathrm{dt}} = -\gamma \int_\Gamma |\nabla_p H + T \nabla_p \log \rho|^2 \rho \mathrm{dV} \quad ,
\tag{4.36}
$$

which clearly shows that F decreases with time, as expected.

4.2.2   Stationary points for free energy

Let us consider $\rho = Ce^{-\frac{H}{T}} \sigma$, with $\sigma = 1 + \eta$. This is the same out-of-equilibrium measure we defined in section 4.1.1. We already noticed from equation (4.36) that the free energy follows the behaviour we expect: it decreases. What we want to make sure of is that F keeps decreasing until the system reaches equilibrium, instead of settling for a constant value beforehand. With some calculation, we can rearrange the formula:

$$
\begin{aligned}
\nabla_p H + T \nabla_p \log \rho \quad &= \quad \nabla_p H + T \nabla_p \big(\log(e^{-\frac{H}{T}} \sigma) \big) = \\
&= \quad \nabla_p H - \nabla_p H + T \nabla_p \log \sigma = T \frac{\nabla_p \sigma}{\sigma} \quad ,
\end{aligned}
\tag{4.37}
$$

therefore,

$$
\frac{\mathrm{d}F}{\mathrm{dt}} = -\gamma \int \frac{|T \nabla_p \sigma|^2}{\sigma^2} \sigma \, \mathrm{d}\mu_{\mathrm{eq}} = -\gamma T^2 \int \frac{|\nabla_p \sigma|^2}{\sigma} \, \mathrm{d}\mu_{\mathrm{eq}} \quad .
\tag{4.38}
$$

Knowing that

$$\nabla_p(\sqrt{\sigma}) = \frac{\nabla_p \sigma}{2\sqrt{\sigma}} \quad , \tag{4.39}$$

we obtain

$$\frac{\mathrm{d}F}{\mathrm{d}t} = -4\gamma T^2 \int |\nabla_p(\sqrt{\sigma})|^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad . \tag{4.40}$$

One can easily see that in the case of a mechanical system of Hamiltonian (4.15), it is possible to use the Poincarè inequality for gaussian measures once again. To simplify the notation, we will assume that all particles bear the same mass; such restriction is easily generalized to the case of different masses. Keeping in mind the calculations made in section 4.1.3 regarding the constant for the inequality, we have that

$$\int |\nabla_p(\sqrt{\sigma})|^2 \, \mathrm{d}\mu_{\mathrm{eq}} \geq \frac{N}{mT} \mathrm{Var}(\sqrt{\sigma}) \quad , \tag{4.41}$$

so,

$$\frac{\mathrm{d}F}{\mathrm{d}t} \leq -\frac{4\gamma TN}{m} \mathrm{Var}(\sqrt{\sigma}) \quad . \tag{4.42}$$

This means that the free energy can be stationary only when $\mathrm{Var}(\sqrt{\sigma}) = 0$. But since

$$\mathrm{Var}(\sqrt{\sigma}) = \int (\sqrt{\sigma} - \langle\sqrt{\sigma}\rangle)^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad , \tag{4.43}$$

this is true iff $\sqrt{\sigma} = const.$ almost everywhere, which implies that η must also be constant almost everywhere. In section 4.1.1 we saw that η si a function of mean zero; so

$$\int \eta \, \mathrm{d}\mu_{\mathrm{eq}} = 0 \quad \Rightarrow \quad \eta = 0 \quad . \tag{4.44}$$

We just showed that the only stationary moment for the free energy is the one in which the probability density ρ of the system is precisely the Gibbs canonical density. So, as we expected from well known theorems of statistical mechanics, the free energy in this kind of system decreases during its evolution until equilibrium is reached.

4.2.3 Internal energy

After analyzing the temporal behaviour of the free energy, let us look at the internal energy of the system

$$U(\rho) = \langle H\rangle_\rho = \int_\Gamma H\rho\mathrm{dV} \quad . \tag{4.45}$$

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We are not going to enter too deep in a dissertation about this quantity as we did with the free energy; instead, we are simply going to study its time derivative and determine that the Gibbs density provides a good stationary point for the internal energy. Therefore, we have:

$$\frac{\mathrm{d}U}{\mathrm{dt}} = \int H \frac{\partial \rho}{\partial t} \mathrm{dV} = -\int H\{\rho, H\}\mathrm{dV} + \int H\nabla_p \cdot (\gamma \rho \nabla_p H)\mathrm{dV} + D\int H\Delta_p \rho \mathrm{dV} \quad (4.46)$$

Studying each term of the above equation, and remembering that we are always working with a ρ that vanishes at infinity - so we apply the divergence theorem when needed- , we find:

$$-\int H\{\rho, H\}\mathrm{dV} = -\int H\nabla\rho \cdot J\nabla H \mathrm{dV} = -\frac{1}{2}\int \nabla\rho \cdot J\nabla(H^2)\mathrm{dV} =$$

$$= -\frac{1}{2}\int \nabla \cdot (\rho J\nabla(H^2))\mathrm{dV} = 0 \quad ; \qquad (4.47)$$

$$\int H\nabla_p \cdot (\gamma\rho\nabla_p H)\mathrm{dV} = \int \nabla_p \cdot (\gamma\rho H\nabla_p H)\mathrm{dV} - \gamma\int |\nabla_p H|^2 \rho\mathrm{dV} =$$

$$= -\gamma\int |\nabla_p H|^2 \rho\mathrm{dV} \quad ; \qquad (4.48)$$

$$D\int H\Delta_p \rho\mathrm{dV} = D\int \nabla_p \cdot (H\nabla_p \rho)\mathrm{dV} - D\int \nabla_p H \cdot \nabla_p \rho\mathrm{dV} =$$

$$= -D\int \nabla_p \cdot (\rho\nabla_p H)\mathrm{dV} + D\int \rho\Delta_p H\mathrm{dV} =$$

$$= D\int \rho\Delta_p H\mathrm{dV} \quad ; \qquad (4.49)$$

so, overall, the time derivative of the internal energy reads:

$$\frac{\mathrm{d}U}{\mathrm{dt}} = -\gamma\int_\Gamma |\nabla_p H|^2 \rho\mathrm{dV} + D\int_\Gamma \Delta_p H\rho\mathrm{dV} \quad . \qquad (4.50)$$

As previously said, we'd like to find that the time derivative of the internal energy gives zero at equilibrium, being equilibrium itself a stationary state. It is very easy to check that everything goes as expected. If one takes $\rho_{eq} = e^{-\frac{H}{T}}$, and applies the same instruments used before, one finds:

$$-\gamma\int_\Gamma |\nabla_p H|^2 \rho\mathrm{dV} = \gamma T\int_\Gamma \nabla_p \rho_{eq} \cdot \nabla_p H\mathrm{dV} \qquad (4.51)$$

$$D\int_\Gamma \Delta_p H\rho\mathrm{dV} = -\gamma T\int_\Gamma \nabla_p \rho_{eq} \cdot \nabla_p H\mathrm{dV} \quad , \qquad (4.52)$$

as expected. The Gibbs probability provides, indeed, a valid environment for the internal energy to be in a stationary state.

In the our current case, in which we know something more about the Hamiltonian (i.e. the form of its kinetic part $K(p)$), we can discuss the topic further. Let us work with N particles of the same mass in a three-dimensional system. One can see that:

$$(\nabla_p H)_i = \frac{p_i}{m} \quad , \tag{4.53}$$

where i indicates the i-component out of $3N$ total components. Therefore, it follows:

$$|\nabla_p H|^2 \;=\; \sum_i^{3N} \frac{p_i^2}{m^2} = \frac{2}{m} K(p) \quad , \tag{4.54}$$

$$\Delta_p H \;=\; \sum_i^{3N} \frac{1}{m} = \frac{3N}{m} \quad . \tag{4.55}$$

Naming $\langle K \rangle$ the mean value of the kinetic energy with respect to the measure $d\mu = \rho dV$, we have

$$\frac{dU}{dt} = -\frac{2\gamma}{m} \left(\langle K \rangle - \frac{3}{2} NT \right) \quad . \tag{4.56}$$

Thus, we see that at equilibrium the mean value of the kinetic energy is, as one obviously expects from the equipartition theorem, $\frac{3}{2} N K_B T$.

Chapter 5

Restricted noise

Up until now we worked with a model which considered all the particles in the system to be thermally active, as we put the stochastic component and the dissipation on all degrees of freedom. One can see that this is very seldom the case we encounter everyday. Think of a solid body immersed on a hot medium: the internal particles of the object will not be affected, at first, by the thermal bath, as the only ones in contact with it (i.e. exchanging energy with it in a somewhat random fashion) are the ones on the surface. The same is true if we think of a long object with just one end in contact with the bath. A finer model for nature is then one which considers the thermal agitation only on a restricted number of particles; in our case, this translates in stochastic noise and dissipation only present on a restricted set of degrees of freedom. We will see that the dissertation is almost identical to the one previously done, with only minor adjustments.

5.1   Fokker-Planck in case of restricted noise

To study the case of noise only present on a fraction of particles, i.e. number of degrees of freedom, we first of all need to see how the Fokker-Planck equation presents itself in this case. Following the same steps we did in section 2.3, we apply the noise and the dissipative term only on a restricted set of p-components. To make notation simpler, we will assume that the degrees of freedom that interest us are the last n ones (out of N), which we will indicate with a $\sim$. In any other case, one can just swap indexes with no consequences. Then we have

$$X = X_H - \gamma \begin{bmatrix} 0 \\ \nabla_{\tilde{p}} H \end{bmatrix} = \begin{bmatrix} \nabla_p H \\ -\nabla_q H \end{bmatrix} - \gamma \begin{bmatrix} 0 \\ \nabla_{\tilde{p}} H \end{bmatrix} \quad , \tag{5.1}$$

$$G = \begin{bmatrix} \mathbb{0}_{N-n} & \mathbb{0}_n \\ \mathbb{0}_n & 2D\mathbb{1}_n \end{bmatrix} \quad . \tag{5.2}$$

It is easy to see that the calculation we previously made still hold in this case, with minumum alterations. The Fokker-Planck equation simply reads

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\} + \nabla_{\tilde{p}} \cdot (\gamma \rho \nabla_{\tilde{p}} H) + D \Delta_{\tilde{p}} \rho \quad , \tag{5.3}$$

and the Einstein relation stays the same.

5.2 Mechanical systems

Since the Fokker-Planck equation is of the same form of the one used in Chapter 4, we can study the problem of the approach to equilibrium in the same exact way we did then, i.e. considering the density ρ which describes the system in a state of non-equilibrium, and computing the norm of the deviation from equilibrium, η. The steps are equal to the ones done before, with the exception that each time we saw the derivation with respect to the p-components (∇_p), now we find a derivation with respect to the only p-components on which we put the stochastic and dissipative terms ($\nabla_{\tilde{p}}$). Therefore,

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \frac{\eta^2}{2} \, \mathrm{d}\mu_{\mathrm{eq}} = -\gamma T \int |\nabla_{\tilde{p}} \eta|^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad , \tag{5.4}$$

so that the integral now does not split into N integrals like earlier, but into n, the number of our preferred particles. From now on we will consider particles of same mass m; keep in mind that if one wants to generalize to different masses, one must know the mass of each particle that we decided to thermostate, which could be, in a real physical system, a bit more complicated than the case with all particles thermostated. Consequently, we have

$$\frac{\mathrm{d}}{\mathrm{d}t} \int \eta^2 \, \mathrm{d}\mu_{\mathrm{eq}} \leq -\frac{2\gamma n}{m} \int \eta^2 \, \mathrm{d}\mu_{\mathrm{eq}} \quad , \tag{5.5}$$

and

$$\int \eta^2 \, \mathrm{d}\mu\mathrm{eq} \leq A e^{-\frac{2\gamma n}{m} \cdot t} \quad . \tag{5.6}$$

Thus, the estimated time of equilibrium is now

$$\tau_{eq} \leq \frac{m}{2\gamma n} \quad . \tag{5.7}$$

Being $n < N$, the superior limit just found clearly shows an expected behaviour: the less particles are in contact with the thermal bath, the longer the system will take to reach equilibrium.

Limits for γ

Let us see in this case if we can still make the same observations about how to let γ approach zero in a way that doesn't make our results meaningless. Suppose we want to see what happens in a physical object if we assume that the contact with the thermal bath involves only the particles at its border; if we have a three-dimensional object, and suppose that the density of particles is everywhere uniform, then we have that

$$n \propto N^{2/3} \quad . \tag{5.8}$$

This means that we can still make an argument like the one we did in section 4.1.4, and set γ in a proper way. Just so,

$$\gamma \propto N^{-2/3} \quad , \tag{5.9}$$

and for $N \to \infty$ we have $\gamma \to 0$ without losing a significant superior limit for the time constant. This argument is still valid if we want to study a flat object, i.e. a two-dimentional body, in which

$$n \propto N^{1/2} \quad . \tag{5.10}$$

Different is the case of a one-dimentional body; think about a string of material in which just one end is in contact with a heating source. In this case, unfortunately, we find that

$$n \propto 1 \quad , \tag{5.11}$$

and we can't let γ tend to zero without having the estimation of the time constant approach infinity. This is clearly a pathological case; on the other hand, one dimentional situations are almost always unusual and bizarre, and we shall not worry about it.

Free energy

Exactly like before, the only change to be made in the procedure of Chapter 4, section 4.2, is $p \to \tilde{p}$; we obtain

$$\frac{\mathrm{d}F}{\mathrm{d}t} \leq -\frac{4\gamma Tn}{m} \operatorname{Var}(\sqrt{\sigma}) \quad , \tag{5.12}$$

and the conclusions we draw are the same.

Chapter 6

Conclusions

In this dissertation, our main goals have been covered: we were able to prove that the Fokker-Planck equation ultimately leads to equilibrium, and to provide an evaluation of how long it takes for the system to become stable; also, we could do the same when trying to better resemble the physical system, namely considering agitation only on borderline particles. Nevertheless, many doors still remain open to discussion. Let us briefly examine some of them, explaining why those topic were not faced in this thesis.

Strange Hamiltonians

We always mentioned classic Hamiltonians for our system, which consider separately the momentum components making up the kinetic energy and the position component, present only in the potential energy term. In physics, there are many other systems to be studied whose Hamiltonian is not of said appearance. How does the system behave in that case? Can we still infer that it will reach equilibrium? Does our model tell us? We first thought to benefit from the Brascamp-Lieb inequality mentioned in Chapter 3.2, but the fact that our noise is only present on momenta makes things a little more difficult. Retracing the steps we did to shift from the Brascamp-Lieb inequality to a Poincarè-like inequality, if we take the Hamiltonian in the place of the function $V(x)$ of section 3.2, then we require that $H(q,p) - 2\lambda \mathbb{1}$ be a convex function *with respect to the p-components*. Assuming that $H(q,p)$ is no more than quadratic on the p, we still have that its second derivative with respect to p is generally a function of q. Therefore, the eigenvalues θ_i of its Hessian, which we want to be greater than some constant, will depend on q. To find the constant

needed to complete the inequality we have to use

$$\sup_{i,q} \frac{1}{\theta_i(q)} \leq \frac{1}{2\lambda} \quad . \tag{6.1}$$

Of course this requires some troublesome calculation, and the procedure is highly dependent on the system; this is the reason why we decided to leave this discussion out of our project. Theoretically, though, once the constant is assessed, the steps are similar to what we did in the other case. In fact, when we find the integral in $d\mu$, we can split the measure and use $e^{-\frac{H(q,p)}{T}}\,dp$ to apply the inequality, and then merge the measure back together. Thus, no real conceptual problems arise from exotic types of Hamiltonian, and our model appears to work nonetheless.

Quantum mechanics

Being the system a collection of many microscopic particles, one might want to describe the approach to equilibrium with the point of view of quantum mechanics. The process can start with observing that $\nabla_p \cdot f = \{q, f\}$; the Poisson brackets can then be replaced by the commutator via canonical quantization:

$$\{q, f\} \longrightarrow \frac{1}{1\hbar}[\hat{q}, \hat{f}] \quad , \tag{6.2}$$

where all the physical quantities transform into their corresponding operator (for example, ρ becomes the *density matrix*). This is usually source of compatibility problems; for instance, if the function f seen now is the product of two quantities, then the process leads to different results based on the order of the factors - the product, which is commutative for the quantities in classical physics, is not anymore when dealing with operators. Then, which order is the correct one? To answer the question, some non-trivial consideration are to be made, and such dissertation has been omitted from the project.

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