

# THEORETICAL IDEAS IN NONEQUILIBRIUM STATISTICAL MECHANICS

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## Abstract

In the following work are presented and summarized the main ideas of the mathematical physicist David Ruelle in his work about non equilibrium statistical mechanics [1], focusing on the physical aspects of the obtained results. The fundamental idea behind this work is to take into account the *chaotic character* of the microscopic dynamics. First of all we show that the nonequilibrium steady states, in presence of a Gaussian thermostat, are described by *SRB measures*. In terms of these is possible to express the *Gallavotti-Cohen fluctuation theorem*. Then, near to equilibrium, we recover important results like the *fluctuation-dissipation theorem* and the *Onsager reciprocity relations*. These results just mentioned hold so far only for classical systems and they hold without a thermodynamic limit.

**Keywords:** Ruelle, statistical mechanics, nonequilibrium, steady states.

## 1 Setting the Problem

Due to the high degree of mathematical sophistication and the application to physical problems, the equilibrium statistical mechanics has gained a great success. By contrast the progress of nonequilibrium statistical mechanics has been much slower, mostly on dissipative phenomena close to equilibrium. One of the fundamental and very important problem is the difficulty or impossibility, in general, in defining an Entropy Principle for relaxation processes for systems not in thermodynamic equilibrium.

It is well known that, according to the *second law of thermodynamics*, an extensive quantity called *entropy* can be associated to macroscopic systems which are locally in equilibrium. This definition is such that, when the system is isolated, its entropy can only increase with time or stay constant. A strict increase in entropy correspond to an irreversible process, also called *dissipative* because it dissipates mechanical forms of energy into heat. So the purpose of nonequilibrium statistical mechanics is to explain irreversibility on the basis of microscopic dynamics, and to give quantitative prediction for dissipative phenomena.

### 1.1 Thermostats and Nonequilibrium Steady States

Rather than the traditional *approach to equilibrium* point of view of Boltzmann (see below), one can try to produce and study nonequilibrium steady states. To keep a finite system outside of equilibrium we subject it to non-Hamiltonian forces. Thus the microscopic time evolution ( $f^t$ ) which we want to consider is determined by an evolution equation in the phase space  $\mathcal{M}$  of the form:

$$\frac{dx}{dt} = F(x). \quad (1)$$

Since we have no more conservation of energy,  $x(t)$  no longer evolve in a bounded region of phase space, this means that the system will heat up. Indeed, this is what is observed experimentally: dissipative systems produce heat. So it is necessary to introduce the mathematical equivalent of an *ideal thermostat* in order to take up the heat produced by the system but, at the same time, to allow entropy to be produced in the system, without changing under its influence. We replace thus (1) by:

$$\frac{dx}{dt} = F(x) + \Theta(\omega(t), x), \quad (2)$$

where the effect  $\Theta(\omega(t), x)$  of the thermostat depends on the state  $x$  of the small system, and on the state  $\omega(t)$  of the thermostat, but the time evolution  $t \rightarrow \omega(t)$  does not depend on the state  $x$  of the small system. We may think of  $\omega(t)$  as random (corresponding to a random thermostat), but the simplest choice is to take  $\omega$  constant, and use  $\Theta(x) = \Theta(\omega, x)$  to keep  $x(t)$  on a compact manifold  $M$ . For instance if  $M = \{x : h(x) = E\}$ , we may take

$$\Theta(x) = -\frac{F(x) \cdot \text{grad } h(x)}{\text{grad} \cdot h(x) \text{ grad } h(x)} \text{grad } h(x). \quad (3)$$

This is the so-called *Gaussian thermostat*. We assume for the moment that the phase space of our system is reduced by the action of a thermostat to be a compact manifold  $M$ . In this way the evolution equation on  $M$  has the same form as (1), where the vector field  $F$  on  $M$  now describe both the effects of non-Hamiltonian forces and thermostat.

Consider now a probability measure  $m$  on  $M$  with density  $\underline{m}(x)$ , such that  $m(dx) = \underline{m}(x)dx$  is the probability to find the system in a region of volume  $dx$  in the phase space, which becomes  $(f^t)m$  at time  $t$ . So the probability measures

$$\rho = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t d\tau (f^\tau)m, \quad (4)$$

which are invariant under time evolution  $(f^t)$ , are natural candidates to describe *nonequilibrium steady states*.

## 1.2 Entropy Production

Let's recall that the accepted expression for the entropy of equilibrium states is the *Gibbs entropy*

$$S(\underline{m}) = - \int dx \underline{m}(x) \log \underline{m}(x), \quad (5)$$

and it remains reasonable also outside of equilibrium, as information theory for instance would indicate. So the idea is to define the physical entropy by (5). The density of  $\hat{m} = (f^t)m$  is given by:

$$\hat{m}(x, t) = \frac{\underline{m}(f^{-t}x)}{J_t(f^{-t}x)}, \quad (6)$$

where  $J_t$  is the Jacobian determinant of  $f^t$ . We obtain thus

$$S(\hat{m}) - S(\underline{m}) = \int dx \underline{m}(x) \log J_t(x), \quad (7)$$

which is the amount of entropy gained by the system under the action of external forces and thermostat in time  $t$ . The amount of entropy produced by the system and given to the external world in one unit of time is thus ( $J = J_1$ )

$$e_f(m) = - \int m(dx) \log J(x), \quad (8)$$

so the average entropy production in  $t$  units of time is

$$\frac{1}{t} \sum_{k=0}^{t-1} e_f(f^k m) = \frac{1}{t} [S(\hat{m}) - S(\underline{m})], \quad (9)$$

and when  $t \rightarrow \infty$ , according to (1), tends towards

$$e_f(\rho) = - \int \rho(dx) \log J(x) = - \int \rho(dx) \text{div} F(x), \quad (10)$$

which is the entropy production per unit of time in the nonequilibrium steady state  $\rho$ .

We just note that in an Hamiltonian situation, since the volume element is preserved by  $(f^t)$ ,  $J_t = 1$ , and therefore  $S(\widehat{m}) = S(m)$ . So, we have a problem: the entropy seems to remain constant in time. This happens because the Hamiltonian evolution has time reversal invariance. One of the possible ways to go out of this difficulty is presented by Boltzmann and properly discussed in [2]. But, in order to compute explicit calculations and to deal also with situations far away from equilibrium, the approach followed by Ruelle is preferable.

Notice that the entropy (5) is bounded above, so that  $e_f(\rho) \geq 0$ , and in many cases  $e_f(\rho) > 0$ , as we shall see later. It may appear paradoxical that the state  $\rho$  which does not change in time, constantly gives entropy to the outside world. The solution of the paradox is that  $\rho$  is (normally) a singular measure and therefore has entropy  $-\infty$ : the nonequilibrium steady state  $\rho$  is thus a bottomless source of entropy.

## 2 SRB States

An important assumption which has emerged progressively in recent years is to take seriously into account the chaotic character of the microscopic time evolution. In particular, if we assume the *uniform hyperbolicity* (in mathematical terms) or *strong chaoticity* (in physical terms), the states represented by (4) belong to the more general class called *Sinai-Ruelle-Bowen states*.

In the ergodic theory, a Sinai–Ruelle–Bowen (SRB) measure is an invariant measure that behaves similarly to, but is not an ergodic measure. In order to be ergodic, the time average would need to be equal the space average for almost all initial states  $x \in \mathcal{M}$ , with  $\mathcal{M}$  being the phase space. For an SRB measure  $\rho$ , it suffices that the ergodicity condition be valid for initial states in a set  $B(\rho)$  of positive Lebesgue measure.

In order to give a more physical relevance to an SRB measure, we'll give an equivalent definition, assuming for simplicity that the time evolution happens on *Axiom A attractors*, which are an extensively studied class of dynamical systems. Formally this means that the hyperbolicity assumption is restricted only to a subset  $\Omega$  of the manifold  $M$  and  $\Omega$  is a finite union of disjoint compact attractors  $\mathcal{A}$ .

It's reasonable to say that in general the non equilibrium steady states, in presence of a Gaussian thermostat, are represented by SRB states. In fact the study of SRB measures is transformed by use of symbolic dynamics<sup>1</sup> into a problem of statistical mechanics [3]: one can characterize SRB states as *Gibbs states* (or *equilibrium states*) with respect to a suitable constraint (interaction) which can in turn be characterized by a variational principle. To describe this variational principle, first we need the concept of *Sinai-Kolmogorov entropy*  $h_f(\mu)$ , where  $f = f^1$  is the time-1 map for our dynamical system and  $\mu$  is a  $f$ -invariant probability measure on  $\mathcal{A}$ .

Given a partition  $Q = \{Q_1, \dots, Q_k\}$  of  $\mathcal{A}$ , we define the entropy of a partition

$$H(Q) = - \sum_{m=1}^k \mu(Q_m) \log \mu(Q_m). \quad (11)$$

The  $f$ -pullback of  $Q$  is defined as  $f^{-1}Q = \{f^{-1}Q_1, \dots, f^{-1}Q_k\}$  and further, given two partition  $Q$  and  $R$ , their *refinement* is  $Q \vee R = \{Q_i \cap R_j : \mu(Q_i \cap R_j) > 0\}$ . Now we are finally able to define

$$h_f(\mu) = \sup_Q h_f(\mu, Q) = \sup_Q \lim_{N \rightarrow \infty} \frac{1}{N} H\left(\bigvee_{n=0}^N f^{-n}Q\right), \quad (12)$$

where  $\bigvee_{n=0}^N f^{-n}Q$  is the refinement of an iterated pullback. The entropy (12) has the physical meaning of mean information production per time by the system  $(f^t)$  in the state  $\mu$ .

So we say that the  $(f^t)$ -invariant probability measure  $\rho$  is a SRB state if it makes maximum the function

$$\mu \rightarrow h_f(\mu) - \int \mu(dx) \log J^u(x), \quad (13)$$

where  $J^u(x) > 0$  is the *expanding (unstable) Jacobian*, i.e. the volume expansion factor in the unstable manifold, since under the hyperbolicity assumptions the tangent bundle  $TM$  can be split into two

<sup>1</sup>In mathematics, symbolic dynamics is the practice of modeling a topological or smooth dynamical system by a discrete space consisting of infinite sequences of abstract symbols, each of which corresponds to a state of the system, with the dynamics (evolution) given by the shift operator.

invariant subbundles, one of which is contracting and the other is expanding under  $f^t$ . One can show that there is precisely one SRB measure on each attractor  $\mathcal{A}$  and the maximum of (13) is precisely 0.

If  $m$  is a measure on  $M$ , and if its density  $m(x)$  vanishes outside the basin of attraction of an attractor  $\mathcal{A}$ , then the measure  $\rho$ , related to  $m$  by (4), defines the unique SRB measure on  $\mathcal{A}$  and thus represents a natural nonequilibrium steady state. In particular it can be proved that in this case  $h(\rho)$  is equal to the sum of all positive *lyapunov exponents*.

### 3 Gallavotti-Cohen Fluctuation Theorem

It's possible to use the SRB states to make interesting physical predictions. One of these is the asymptotic formula due to Gallavotti and Cohen for fluctuations of the entropy production. The success of this formula supports the philosophy that calculations based on a very strong hyperbolicity assumptions are in agreement with the numerical experiments.

We say that the microscopic time evolution  $(f^t)$ , with  $t \in \mathbb{R}$ , or  $\mathbb{Z}$  is *reversible* if there is a diffeomorphism  $i : M \rightarrow M$  such that  $i \circ i$  is the identity and  $i \circ f^t = f^{-t} \circ i$ . For a system of particles with positions  $x_k$  and momenta  $p_k$  one may take  $i(x_k, p_k) = (x_k, -p_k)$  if the forces are not velocity dependent. In this physical situation one speaks of *microscopic reversibility*: this was an essential ingredient in Onsager's proof of his reciprocity relations, and it is also essential for the fluctuation theorem of Gallavotti and Cohen. It's important to notice that the reversibility assumption for a nonequilibrium steady state should not be interpreted in a deterministic sense (since the system is non-Hamiltonian) but rather in a stochastic one. This is related to the strong chaoticity assumptions and in that case we deal with concepts like *Markov reversibility* and *detailed balance condition*.

Recall now the formula (10) for the average entropy production per unit of time in the nonequilibrium steady state defined by the SRB measure  $\rho$ . For integer  $\tau > 0$ , let

$$\varepsilon_\tau(x) = \frac{1}{\tau e_f} \sum_{k=0}^{\tau-1} \log J(f^k x)^{-1}. \quad (14)$$

This may be interpreted as a dimensionless entropy production rate or phase space contraction rate at  $x$  over time  $\tau$ , such that  $\rho(\varepsilon_\tau) = 1$ . Note that if we have reversibility  $J(ifx) = J(x)^{-1}$ , and this yields:

$$\varepsilon_\tau \circ i \circ f^\tau = -\varepsilon_\tau. \quad (15)$$

The Gallavotti-Cohen theorem is a statement about the fluctuations of  $\varepsilon_\tau$  with respect to the SRB measure  $\rho$  (or equivalently with respect to time).

In mathematical terms the theorem states that, assuming reversibility, there exists  $p^* > 0$  such that if  $|p| < p^*$  and  $\delta > 0$

$$p - \delta \leq \lim_{\tau \rightarrow \infty} \frac{1}{\tau e_f} \log \frac{\rho(\{x : \varepsilon_\tau(x) \in (p - \delta, p + \delta)\})}{\rho(\{x : \varepsilon_\tau(x) \in (-p - \delta, -p + \delta)\})} \leq p + \delta. \quad (16)$$

For the rigorous proof of the theorem using the SRB states see [1].

We note that this result applies *far from equilibrium* (we assume that the time evolution is reversible, but we do not assume that it is close to Hamiltonian). Placing ourselves *close to equilibrium* we could obtain from this theorem a linear response formula known as *fluctuation-dissipation theorem* and the *Onsager reciprocity relations*, as we will see.

#### 3.1 Physical Meaning of the Fluctuation Theorem

We gave a mathematical formulation to the Gallavotti-Cohen theorem, but it's important to show explicitly what is the physical role of this theorem.

The fluctuation theorem, which originated from statistical mechanics, deals with the relative probability that the entropy of a system which is currently away from thermodynamic equilibrium (i.e. maximum entropy) will increase or decrease over a given amount of time. The possibility of a decreasing for an isolated system seems impossible because of the second law of thermodynamics but, since the entropy is a statistical quantity, there should be a non zero probability that the entropy might spontaneously decrease. So the aim of the theorem is to quantify this probability.

Inspection the proof of (16) shows that the theorem compares, in systems away from equilibrium over a finite time  $\tau$ , the probability that the time-averaged irreversible entropy production takes a value  $p$  and the probability that it takes the opposite value  $-p$ , obtaining an exponential in  $p\tau$ :

$$\frac{P(\varepsilon_\tau(x) \approx p)}{P(\varepsilon_\tau(if^\tau x) \approx p)} \approx e^{e_f p \tau}. \quad (17)$$

In other words, for a finite non-equilibrium system in a finite time, the FT gives a precise mathematical expression for the probability that entropy will flow in a direction opposite to that dictated by the second law of thermodynamics.

This means that as the time or system size increases, the probability of observing an entropy production opposite to that dictated by the second law of thermodynamics decreases exponentially.

Note that the FT does not state that the second law of thermodynamics is wrong or invalid. The second law is a statement about macroscopic systems. The FT is more general since it can be applied to both microscopic and macroscopic systems. When applied to macroscopic systems, the FT is equivalent to the Second Law of Thermodynamics.

## 4 Nonequilibrium Near Equilibrium

An isolated macroscopic system which is not subjected to external forces normally evolves towards a macroscopic state of rest corresponding to certain values of thermodynamic variables like the temperature. At the macroscopic level, this state of thermodynamic equilibrium is described by the *microcanonical ensemble* of equilibrium statistical mechanics. Typically we have a phase space  $\mathbb{R}^{2N}$  with an Hamiltonian function  $H(\mathbf{p}, \mathbf{q})$  where  $\mathbf{p} = (p_1, \dots, p_N)$ ,  $\mathbf{q} = (q_1, \dots, q_N)$ , and the so-called microcanonical ensemble corresponding to a certain energy  $E$  is the probability measure:

$$\rho(d\mathbf{p}d\mathbf{q}) = \frac{1}{\omega} \delta(H(\mathbf{p}, \mathbf{q}) - E) d\mathbf{p}d\mathbf{q}, \quad (18)$$

where  $\omega$  is a normalizing constant and it is assumed that  $M = \{(\mathbf{p}, \mathbf{q}) \in \mathbb{R}^{2N} : H(\mathbf{p}, \mathbf{q}) = E\}$  is a smooth compact manifold. Under the *ergodic hypothesis* we can assume  $\rho$  to be ergodic.

At microscopic level we have an Hamiltonian time evolution:

$$\frac{d}{dt} \begin{pmatrix} \mathbf{p} \\ \mathbf{q} \end{pmatrix} = \begin{pmatrix} -\partial_{\mathbf{q}} H(\mathbf{p}, \mathbf{q}) \\ \partial_{\mathbf{p}} H(\mathbf{p}, \mathbf{q}) \end{pmatrix}. \quad (19)$$

Notice that the equilibrium state  $\rho$  is an SRB measure. This assumption will allow us to recover formal results of non equilibrium statistical mechanics close to equilibrium.

### 4.1 Linear Response and Entropy Production

The definition of SRB states extends to nonautonomous systems. This gives in particular the possibility of studying the response of an equilibrium state to small time dependent perturbations. For a more general discussion about linear response of stationary nonequilibrium states see [1] chapter 4.

To give the following definition it will be convenient to assume that we have discrete time  $t \in \mathbb{Z}$ . Instead of a single diffeomorphism  $f$  of the manifold  $M$  we consider a family  $(f_t)_{t \in \mathbb{Z}}$ , i.e. we have time dependent dynamics. In this situation a SRB state is a family of probability measure  $(\rho_t)_{t \in \mathbb{Z}}$  where  $\rho_t$  is a probability measure on  $M$  such that

$$\rho_t = \lim_{n \rightarrow \infty} f_t \dots f_{t-n} \rho, \quad (20)$$

and in particular  $\rho_t = f_t \rho_{t-1}$ . Note that the above situation arises for random dynamical systems, however for applications to physics, it is desirable to be able to consider a nonprobabilistic situation.

Consider now the perturbed time evolution

$$\frac{dx}{dt} = F(x) + \delta_t F(x) \quad (21)$$

on the compact manifold  $M$ . Let  $(\rho + \delta_t \rho)$  be the time dependent SRB state for the evolution (21). We are interested in the response  $(\delta_t \rho)$  to the time dependent perturbation  $(\delta_t F)$ .

It is possible to show that the linear change for the SRB state is given by

$$\delta_t \rho = \int d\tau \kappa_{t-\tau} \delta_\tau F, \quad (22)$$

where the linear operator  $\kappa_\sigma$  is called *response function*, such that  $\kappa_\sigma = 0$  if  $\sigma < 0$  (property of *causality*) and

$$(\kappa_\sigma X)\Phi = - \int \rho(dy) \operatorname{div} X(y) \Phi(f^\sigma y) \quad (23)$$

if  $\sigma \geq 0$ , for a suitable vector field  $X$  and function  $\Phi$ .

Another important definition that we will use later is the *susceptibility*, defined as the Fourier transform of the response function:

$$\tilde{\kappa}_\omega = \int d\sigma \kappa_\sigma e^{i\omega\sigma}. \quad (24)$$

For a small time dependent change  $\delta_t F$  of the vector field  $F$  (with corresponding equilibrium state  $\rho$ ) we shall be able to determine the entropy production to second order.

Remember that, as we have seen, for an equilibrium state the entropy production vanishes, which is therefore described as *nondissipative*. This fact is easily derived from (10) using  $\operatorname{div} F = 0$  (or  $J = 1$ ).

We expand the SRB state corresponding to  $F + \delta_t F$  to second order as  $\rho + \delta_t \rho + \delta_t^{(2)} \rho$ , and compute the corresponding time dependent entropy production. It is possible to show that the term corresponding to  $\delta_t^{(2)} \rho$  does not contribute to the result, which is

$$e_t = \int_0^\infty d\sigma \int \rho(dy) \operatorname{div} \delta_{t-\sigma} F(y) \operatorname{div} \delta_t F(f^\sigma y). \quad (25)$$

As a corollary, it's easy to obtain the expression for the time independent entropy production, i.e. when the perturbation does not depend on time  $t$  ( $\delta_t F = \delta F$ ):

$$e = \frac{1}{2} \int_{-\infty}^\infty d\sigma \int \rho(dy) \operatorname{div} \delta F(y) \operatorname{div} \delta F(f^\sigma y). \quad (26)$$

## 4.2 Onsager Reciprocity Relations

In the last section we have seen the expression for the linear response and entropy production corresponding to a *force*  $X (= \delta F)$  pushing a system far away from equilibrium. A striking feature of the formulae that we have obtained is that  $X$  occurs only in the form  $\operatorname{div} X$ . Nonequilibrium statistical mechanics close to equilibrium is very special because of this feature, which does not persist far from equilibrium.

Let us call *observable* a function  $\Phi : M \rightarrow \mathbb{R}$ . We further assume that  $\Phi$  is smooth and  $\rho(\Phi) = 0$ . Thus, if  $X$  is any smooth vector field,  $\operatorname{div} X$  is an observable, and every observable is the form  $\operatorname{div} X$ .

Let assume that the dynamics ( $f^t$ ) of our system depends smoothly on parameters  $E_\alpha$ , as is natural in physical applications. We also assume that when the parameters  $E_\alpha$  take the value 0 equilibrium is achieved, corresponding to a vector field  $F$ . Close to equilibrium  $F$  is replaced by  $F + \delta F$ , and we take as earlier  $X = \delta F$ . We may thus write, to first order

$$X = \sum_\alpha V_\alpha E_\alpha. \quad (27)$$

We assume here that  $E_\alpha$  are time independent. The *thermodynamic forces* which occur in the formalism of nonequilibrium thermodynamics will now be identified with the  $E_\alpha$ .

We define the *thermodynamic flux* conjugate to  $E_\alpha$  as

$$\mathcal{J}_\alpha = \rho_{F+\delta F} \left( \frac{\partial}{\partial E_\alpha} \sigma_{F+\delta F} \right), \quad (28)$$

where

$$\sigma_{F+\delta F} = -\operatorname{div}(F + \delta F) = -\operatorname{div} X \quad (29)$$

is the local entropy production (recall that  $\operatorname{div} F = 0$ ). To first order in  $X$  the flux is, using (22),(23)

$$\mathcal{J}_\alpha = \sum_{\beta} L_{\alpha\beta} E_\beta, \quad (30)$$

where

$$L_{\alpha\beta} = \int_0^\infty d\sigma \int \rho(dy) \operatorname{div} V_\beta(y) \operatorname{div} V_\alpha(f^\sigma y) \quad (31)$$

are known as the *Onsager phenomenological coefficients*. The definition (30) is such that the entropy production given in (26) is

$$e = \sum_{\alpha} \mathcal{J}_\alpha E_\alpha = \sum_{\alpha\beta} L_{\alpha\beta} E_\alpha E_\beta. \quad (32)$$

Onsager's contribution was to demonstrate that not only  $L_{\alpha\beta}$  is positive semi-definite, it is also symmetric, except in cases where time-reversal symmetry is broken.

Following the idea of Gallavotti and Ruelle in [4], it's possible to give a general proof to these symmetries called *Onsager reciprocity relations*, under the assumption of *microscopic reversibility*, treated previously. Just note that in the equilibrium case the reversibility is not just applied to the dynamics  $f^t$  but also to the equilibrium SRB state  $\rho$ , i.e.  $i\rho = \rho$ . Obviously this is no more true far from equilibrium.

Let assume that there is a (sufficiently large) Banach space  $\mathcal{B}$  of functions  $\Phi : M \rightarrow \mathbb{R}$  such that  $\rho(\Phi) = 0$  if  $\Phi \in \mathcal{B}$ . Assuming reversibility we may define  $\epsilon\Phi = \Phi \circ i$  and, if  $\mathcal{B}$  has a basis  $(\Phi_\alpha)$  such that  $\epsilon\Phi_\alpha = \Phi_\alpha \circ f^t = \epsilon_\alpha \Phi_\alpha$  with  $\epsilon_\alpha = \pm 1$ , then one obtain

$$L_{\alpha\beta} = \epsilon_\alpha \epsilon_\beta L_{\beta\alpha} = L_{\beta\alpha}, \quad (33)$$

which is the usual form of the Onsager reciprocity relations.

Reciprocal relations occur between different pairs of forces and flows in a variety of physical systems. For example, consider fluid systems described in terms of temperature, matter density, and pressure. In this class of systems, it is known that temperature differences lead to heat flows from the warmer to the colder parts of the system; similarly, pressure differences will lead to matter flow from high-pressure to low-pressure regions. What is remarkable is the observation that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow (as in convection) and pressure differences at constant temperature can cause heat flow. Onsager's reciprocity is manifest also in thermoelectric effect since we have the equality between the Peltier (heat flow caused by a voltage difference) and Seebeck (electrical current caused by a temperature difference) coefficients of a material. Similarly, also the so-called "direct piezoelectric" (electrical current produced by mechanical stress) and "reverse piezoelectric" (deformation produced by a voltage difference) coefficients are equal [5].

### 4.3 Fluctuation-Dissipation Theorem

The fluctuation-dissipation theorem is a general result of statistical thermodynamics that quantifies the relation between the fluctuations in a system that obeys to microscopic reversibility and the response of the system to applied perturbations.

The theorem says that when there is a process that dissipates energy, turning it into heat (i.e. friction), there is a reverse process related to thermal fluctuations. A general proof of this theorem was made by Kubo in [6], but an important antecedent to the general theorem is the Einstein's explanation of *Brownian motion*. In fact he noted that the same random forces that cause the erratic motion of a particle in Brownian motion would also cause drag if the particle were pulled through the fluid. In other words, the fluctuation of the particle at rest has the same origin as the dissipative frictional force one must do work against, if one tries to perturb the system in a particular direction.

Let's define, for  $A, B \in \mathcal{C}(M, \mathbb{C})$ , the *time correlation function* as

$$\rho_{AB}(t-s) = \rho((A \circ f^s)(B \circ f^t)) - \rho(A)\rho(B). \quad (34)$$

Thus is possible to show that the time autocorrelation function  $\rho_{AA}$  is the Fourier transform of a positive density  $\tilde{\rho}_{AA}(\omega)$ , called *spectral density*, or *power spectrum* of the "signal"  $t \rightarrow A \circ f^t$ , so

$$\rho_{AA}(\tau) = \int d\omega e^{i\omega\tau} \tilde{\rho}_{AA}(\omega). \quad (35)$$

Recalling the definition of susceptibility in (24), for the SRB measure  $\rho$  in the equilibrium state the theorem can be expressed as

$$\frac{1}{2}[(\tilde{\kappa}_{\omega}(-\text{div}X))\Phi + (\tilde{\kappa}_{-\omega}(-\text{div}X))\Phi] = \tilde{\rho}_{(-\text{div}X),\Phi}(\omega), \quad (36)$$

i.e. the real part of the susceptibility corresponding to the force  $X$  is given by the Fourier transform of a time correlation function for the equilibrium state  $\rho$ . The left-hand side corresponds to dissipation (the nonequilibrium process associated with  $X$ ) and the right-hand side to fluctuation (in the equilibrium state). We note that the physical use of the above formula requires that we can identify  $-\text{div}X$  as an observable, as we already discussed.

## 5 Other Considerations and Conclusion

The view of nonequilibrium statistical mechanics presented previously was based on chaotic microscopic dynamics. In particular we have restricted ourselves to classical systems, having little to say about the quantum case. In order to obtain a nonequilibrium steady state we subjected a finite system to non-Hamiltonian forces: a typical example is the system  $\Sigma$  shown in Fig. (1).  $\Sigma$  consists of classical particles confined to a solid torus, and having ordinary (Hamiltonian) interactions with each other and with scatterers. Furthermore the particles are charged and pushed around the torus by an electric field  $\mathcal{E}$  associated locally with a potential  $U$ . In fact the electric potential is multivalued, and changed by an additive constant after one turn around the solid torus. Finally the system is thermostatted by fixing the total kinetic energy of the particles.

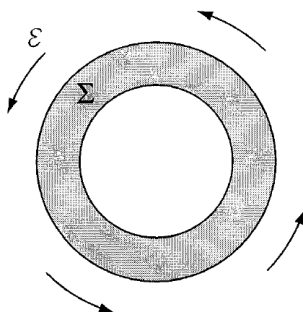


Figure 1: Example of a Non-Hamiltonian system with Gaussian thermostat.

Using these SRB measures as nonequilibrium steady states we expressed the important *Gallavotti-Cohen fluctuation theorem* and then, near to equilibrium, we recovered correctly the *fluctuation-dissipation theorem* and the *Onsager reciprocity relations*.

Unfortunately, the nice results obtained for finite classical systems with non-Hamiltonian forces seem difficult to extend to the quantum situation. Indeed, the Schrodinger equation requires a true potential function, not a multivalued one. One may also remark that if SRB states can forever produce entropy, it is because their own entropy is  $-\infty$ . A quantum analog of this situation seems hard to achieve, because quantum entropies are positive.

### 5.1 Thermodynamic Limit

We just conclude with a discussion about the thermodynamic limit: remark that the obtained results are valid without this limit and we want to justify this fact briefly.

Statistical mechanics deals mostly with macroscopic systems, and some important phenomena like phase transitions make sense only in the large system limit. At a technical level, an important feature of the large system limit (thermodynamic limit) in equilibrium statistical mechanics is the equivalence



of ensembles. Roughly speaking, this corresponds to the fact that for large systems, extensive variables usually fluctuate very little.

The notion that extensive variables often do not fluctuate much in nonequilibrium statistical mechanics (with the microcanonical ensemble replaced by the SRB measure) probably has some validity, but a firm theoretical basis is lacking. There are also some danger signs coming from physics. Suppose for instance that we try to produce a nonequilibrium steady state corresponding to homogeneous shear in a fluid. Macroscopic fluid theory tells us that the homogeneous shear flow that we try to produce is unstable and will become turbulent with, presumably, fluctuations on all scales.

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