Fluctuation Theorem and Chaos

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February 28, 2008

Abstract

The heat theorem (i.e. the second law of thermodynamics or the existence of entropy) is a manifestation of a general property of hamiltonian mechanics and of the ergodic Hypothesis. In nonequilibrium thermodynamics of stationary states the chaotic hypothesis plays a similar role: it allows a unique determination of the probability distribution (called SRB *distribution on phase space providing the time averages of the observables. It also implies an expression for a few averages concrete enough to derive consequences of symmetry properties like the fluctuation theorem or to formulate a theory of coarse graining unifying the foundations of equilibrium and of nonequilibrium.*

1 Boltzmann's Heat Theorem

In equilibrium statistical mechanics states are identificed with time invariant probability distributions μ on phase space. Thermodynamic functions, identified with time averages of mechanical observables, are expressed as integrals $\langle F\rangle$ of suitable mechanical obeservables F. The averages depend on control parameters $\boldsymbol{\alpha}$, like volume, energy, kinetic energy. Under changes b $d\boldsymbol{\alpha}$ of the control parameters the thermodynamic quantities change so that the variation of the average energy and the variation of the volume are dU and dV and are related to the time averages of the kinetic energy $\langle K\rangle \stackrel{def}{=} \langle\sum_{i=1}^N \frac{m\dot{\mathbf{x}}_i^2}{2}\rangle \stackrel{def}{=} \frac32 N k_B T$ and of $p \stackrel{def}{=} \langle -\partial_V U\rangle$, with U being the total potential energy, so that, expressing p, T in terms of the control parameters:

Heat Theorem: (HT) *Changing* $\boldsymbol{\alpha}\to\boldsymbol{\alpha}+d\boldsymbol{\alpha}$ *induce changes* dU, dV, *with*

$$\frac{dU + pdV}{T} = \text{exact} \stackrel{def}{=} dS, \tag{1.1}$$

under the ergodic hypothesis, or equivalently under the assumption that the distributions μ are elements of one among the classical ensembles, like microcanonical, canonical,. . . ,[1, 2].

In modern terminology: the *ergodic hypothesis* (EH) implies equilibrium statistical mechanics. The guiding idea is that HT holds for *all* (ergodic) systems with Hamiltonian of the form $H = K + U$: *whether having few* ($\sim$ 1) *or many* ($\sim 10^{19}$) *degrees of freedom*, as long as EH holds. This means that HT is a trivial consequence of the Hamiltonian structure of the mechanical systems describing the microscopic motions. It is always valid, like a *symmetry property*, and it is highly nontrivial in systems with many degrees of freedom, being the second law of thermodynamics. In other words a guiding idea to understand certain universal laws is that they merely reflect symmetries or general stuctures, of the underlying equations, which may have deep consequences in large systems: e.g, via the HT, the roots of second law can be found, [1], in the simple properties of the pendulum.

2 Thermostats and reversiblity

Stationary states out of equilibrium are realized when on a system are present staionary currents. In such systems currents generate, by dissipation, heat that is absorbed by thermostats.

Recent progress has been achieved by employing simple models of the thermostats with the feature of being *finite* systems of particles, hence well suited for simulations. There are various types of thermostats considered in the literature. As a rather general class of thermostats model consider

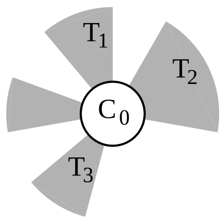

Fig.1: $\mathcal{C}_0$ ("system") interacts with shaded T_j ("thermostats") constrained to keep fixed kinetic energy $K_j = \frac{m}{2}\dot{\mathbf{X}}_j^2 = \frac{3}{2}N_j k_B T_j$.

The equations of motion for the $N_0, N_1, \ldots$ particles located in configurations $\mathbf{X} = (\mathbf{X}_0, \mathbf{X}_1, \ldots)$ inside the containers $\mathcal{C}_0, T_1, \ldots$ (if here $\mathbf{X}_j =$

$(\mathbf{x}_{j,1},\ldots,\mathbf{x}_{j,N_j})$ will be (as an example with all masses equal), $\mathbf{E}=$ positional "stirring forces", U_j internal energy in the j-th container, $W_{0,j}$ potential energy of interaction between the particles in $\mathcal{C}_0$ and those in $\mathcal{C}_j$)

$$\begin{aligned} m\ddot{\mathbf{X}}_0 =& -\partial_{\mathbf{X}_0}\Big(U_0(\mathbf{X}_0)+\sum_{j>0}W_{0,j}(\mathbf{X}_0,\mathbf{X}_j)\Big)+\mathbf{E}(\mathbf{X}_0),\\ m\ddot{\mathbf{X}}_i =& -\partial_{\mathbf{X}_i}\Big(U_i(\mathbf{X}_i)+W_{0,i}(\mathbf{X}_0,\mathbf{X}_i)\Big)-\alpha_i\dot{\mathbf{X}}_i \end{aligned} \tag{2.1}$$

The energies $U_0, U_j, W_{0,j}$ should be imagined as generated by pair potentials $\varphi_0,\varphi_j,\varphi_{0,j}$ short ranged, smooth, or with a singularity like Lennard-Jones type at contact, and by external potentials modeling the containers walls), α_i determined so that $K_i=\frac32 N_i k_B T_i \equiv$ *const*.

More generally thermostats can even act on regions of $\mathcal{C}_0$: eg. in electric conduction models analogous to Drude's model (1899!), one imagines that the collisions with the lattice communicate energy to the lattice vibrations ("phonons") and this is modeled by adding a constraint that $\frac{m}{2}\dot{\mathbf{X}}_0^2=\frac32 k_B T_0$ keeping the total kinetic energy of the N_0 particles in $\mathcal{C}_0$ identically constant realized by an extra term $-\alpha_0\dot{\mathbf{X}}_0$ in the first of Eq.(2.2) with α_0 suitably chosen. The multipliers α_j in Eq.(2.2) are readily computed by imposing constancy of $K_i\equiv const \stackrel{def}{=} \frac32 N_i k_B T_i$ and are

$$\alpha_i \equiv \frac{Q_i-\dot{U}_i}{3N_i k_B T_i} \tag{2.2}$$

and $Q_i\equiv$ work per unit time done by $\mathcal{C}_0$ on $\mathcal{C}_i$:

$$Q_i \stackrel{def}{=} -\dot{\mathbf{X}}_i\cdot\partial_{\mathbf{X}_i}W_{0,i}(\mathbf{X}_0,\mathbf{X}_i) \tag{2.3}$$

and it is naturally interpreted as the *heat* ceded per unit time to the thermostat $\mathcal{C}_i$.

The main feature of the above equations is that they are *not* Hamiltonian and, therefore, the phase space volume measured by the divergence $\sigma(\mathbf{X},\dot{\mathbf{X}})$ is not zero, and after an algebraic computation is checked to be (neglecting for simplicity factors of the form $(1-\frac{1}{3N_j})$)

$$\begin{aligned} &\sigma(\mathbf{X},\dot{\mathbf{X}})\equiv\varepsilon(\mathbf{X},\dot{\mathbf{X}})+\dot{W}(\mathbf{X}),\\ &\varepsilon(\mathbf{X},\dot{\mathbf{X}})=\sum_{j=1}^{n}\frac{Q_j}{k_B T_j},\quad W=\sum_j\frac{U_j(\mathbf{X}_j)}{k_B T_j} \end{aligned} \tag{2.4}$$

This is a sum of two terms, one of which has the interpretation of entropy increase of the thermostats per unit time while the other is a time derivative. Therefore one term is accessible not only in simulations but it is also conceivable that it can be measured in experiments; the other is instead strongly model dependent, coordinates dependent and metric dependent.

Abridging often $(\mathbf{X},\dot{\mathbf{X}})$ simply by x and changing coordinates or metric the expression for σ changes as $\sigma'(x) = \sigma(x) + \frac{d}{dt}\Gamma(x)$ with a suitable Γ. Therefore *only* time averages over long times can have "intrinsic" meaning because

$$\frac{1}{\tau}\int_0^\tau \sigma'(S_t x)dt = \frac{1}{\tau}\int_0^\tau \sigma(S_t x)dt + \frac{\Gamma(S_\tau x)-\Gamma(x)}{\tau} \tag{2.5}$$

so that the two averages of σ and σ' have the same limiting behavior as $\tau\to\infty$, at least if Γ is bounded. Hence if the U_j are bounded (as we shall suppose for simplicity) and if the average $\sigma_+ \stackrel{def}{=} \lim_{\tau\to+\infty}\frac{1}{\tau}\int_0^\tau \sigma(S_t x)$ exists then it can be identified to entropy creation rate

$$\sigma_+ = \langle\sum_j \frac{Q_j}{k_B T_j}\rangle. \tag{2.6}$$

Furthermore the probability distributions in the stationary states of the averages of σ and ε over finite time τ coincide asymptotically as $\tau\to\infty$ because

$$\frac{1}{\tau}\int_0^\tau \sigma(S_t x)dt \equiv \frac{1}{\tau}\int_0^\tau \varepsilon(S_t x)dt + \frac{W(\tau)-W(0)}{\tau} : \tag{2.7}$$

for large τ the averages of σ and ε have the *same fluctuations statistics.* Not just the same average: $\langle\sigma\rangle\equiv\langle\varepsilon\rangle$.

Hence *a general theory of fluctuations of long time averages of* σ*, if at all possible, will imply a general theory of fluctuations of* ε. And the latter is a quantity accessible experimentally via calorimetric and thermometric measurements without need of the equations of motion.

A further *important feature* of the model is that its equations, Eq.)2.1), have a *time reversal symmetry.* This means that there exists a map I of phase space which is isometric and smooth with $I^2 = 1$ and $IS_t = S_{-t}I$ if $t\to S_t(\mathbf{X},\dot{\mathbf{X}})$ denotes the solution to the equations of motion with initial datum $(\mathbf{X},\dot{\mathbf{X}})$, $\mathbf{X}\stackrel{def}{=}(\mathbf{X}_0,\mathbf{X}_1,\ldots)$. In this case I can be simply defined as $I(\mathbf{X},\dot{\mathbf{X}})\stackrel{def}{=}(\mathbf{X},-\dot{\mathbf{X}})$.

3 Chaotic hypothesis

Having identified entropy creation rate with a microscopic mechanical quantity has been a key step towards the understanding of nonequilibrium steady states. In a way it might turn out to be as important as the realization, marking the beginning of statistical mechanics, that in equilibrium the average kinetic energy has to be identified with the absolute temperature.

To turn the above "discovery", [3, 4], into a few quantitative predictions of properties of steady nonequilibrium states it is necessary to identify the probability distributions on phase space that can be used to yield the ime averages of the observables.

The difficulty is that unless $\sigma_+ = 0$, Eq.(2.6), such probability distributions must give probability 1 to a set of data which has 0 volume. This kind of problem arose in the theory of turbulence and was solved by Ruelle's proposal, [5], that the system (for instance the Navier Stokes evolution) is so chaotic that it can be regarded as having an axiom A attractor.

The idea has been extended to the dynamics of thermostatted systems. It is convenient to formulate it in terms of a map S between *timing events*, i.e. by imagining to perform observations every time a prefixed event takes place or, mathematically, every time the trajectory crosses a prefixed surface Σ in phase space. The time evolution can then be described by a map S defined on Σ and mapping an $x \in \Sigma$ into the next point Sx where the trajectory of x crosses again Σ ("*Poincaré's map* on Σ"). In this case the phase space contraction is the logarithm of the Jacobian determinant of the map S: namely $\widetilde{\sigma}(x) \stackrel{def}{=} -\log|\det \partial S(x)|$.

It should be remarked that the time between two successive events is in general variable as a function of the point x: calling it $t(x)$ the map S and the solutions $t \to S_t x$ of the equations of motion are related by $Sx \equiv S_{t(x)}x$ and therefore for $x \in \Sigma$ it is $\widetilde{\sigma}(x) = \int_0^{t(x)} \sigma(S_t x)dt$, and $\int_0^\tau F(S_t x)dt = \sum_{k=0}^N \widetilde{F}(S^k x)$.

The mentioned extension is obtained by formulating the

Chaotic hypothesis (CH) *Motions developing on the attracting set for map S representing the evolution of a chaotic system of particles, observed in discrete time via a choice of timing events Σ, may be regarded as motions of transitive hyperbolic system.*

Informally such a system (also called *Anosov system*) has a dynamics with the property that following the motion of any initial datum x the nearby points separate from it exponentially fast, in the future *and* in the past, except when located on a surface $W_s(x)$ through x or, respectively, on another surface $W_u(x)$.

The assumption has to be understood in the same sense as the EH: the latter, as in RUELLE's view in [6], can be commented as "*... while one would be very happy to prove ergodicity because it would justify the use of Gibbs' microcanonical xensemble, real systems perhaps are not ergodic but behave nevertheless in much the same way and are well described by Gibbs' ensemble...*".

Under the CH the following properties hold:

(1) there is a *unique* distribution μ such that, for all x outside a set of *zero volume*,

$$\lim_{N\to\infty}\frac{1}{N}\sum_{k=0}^{N-1}F(S^kx)=\int\mu(dy)F(y). \tag{3.1}$$

(2) the probability distribution μ has an "explicit" expression "similar to the equilibrium Gibbs distribution", [7].
(3) μ is concentrated on a 0 volume "attractor".

The distribution μ is called the "SRB distribution" (acronym for Sinai-Ruelle-Bowen). Because of the above properties Anosov maps are considered a *paradigm of chaos*, much as harmonic oscillators are considered paradigms of *order*. They enjoy several interesting properties. Consider the finite time average $f\stackrel{def}{=}\frac{1}{N}\sum_{k=0}^{N-1}F(S^kx)$, then

Fluctuation Law: *There are values f_1, f_2 such that f is in $[a,b]\subset(f_1,f_2)$ with μ-probability $Prob_\mu(f\in[a,b])\sim e^{\tau\zeta_F(f)}$ in the sense that*

$$\lim_{N\to\infty}\frac{1}{N}\log Prob_\mu(f\in[a,b])=\max_{f\in[a,b]}\zeta_F(f), \tag{3.2}$$

and $\zeta_F(f)$ is analytic and convex in (f_1,f_2).
More generally,[8], given n observables $\mathbf{F}=(F_1,\ldots,F_n)$, there exists a convex open set $\Gamma\subset R^m$, $m\le n$, with the property that if $\Delta\subset\Gamma$ is a closed set and $f_j\stackrel{def}{=}\frac{1}{N}\sum_{k=0}^{N-1}F_j(S^kx)$, then

$$Prob_\mu(\mathbf{f}\in\Delta)=Prob_\mu((f_1,\ldots,f_n)\in\Delta)\propto_{\tau\to\infty}e^{\tau\max_{\mathbf{f}\in\Delta}\zeta(\mathbf{f})} \tag{3.3}$$

with $\zeta_{\mathbf{F}}$ analytic and convex in Γ. (Sinai, [9]).

The function $\zeta_{\mathbf{F}}$ is a kind of thermodynamic function and via the mentioned expression of μ it is possible to obtain an explicit (generally "uncomputable") expression of stationary averages $\langle F\rangle_\mu$ and of $\zeta_{\mathbf{F}}$.

4 Fluctuation Theorem

Consider time reversal symmetric evolutions, see Sec.2. If the dynamics is a discrete one, associated with a Poincaré section Σ and a time reversal symmetric evolution, a time reversal symmetry I will be smooth map I of Σ with the properties $I^2=1$ and $IS=S^{-1}I$. It can be obtained by restricting to the timing events map the symmetry in continuous time provided the Poincaré section Σ is chosen so that $I\Sigma=\Sigma$ (just replace Σ by $\Sigma\cup I\Sigma$).

Assume :
(1) *chaotic hypothesis*
(2) *dissipativity*, i.e. the average phase space contraction σ_+, in Eq(2.6), is positive, $\sigma_+>0$, **and**
(3) *time reversal symmetry* by a map I.

Let $F_1\equiv\frac{\sigma}{\sigma_+}$ and $p\stackrel{def}{=}f_1=\frac{1}{N}\sum_{k=0}^{N-1}\frac{\sigma(S^kx)}{\sigma_+}$ where $\sigma(x)\stackrel{def}{=}-\log|\det\partial S)|$. Then, [10, 11],

Fluctuation Theorem (FT): *There is $p^*\ge 1$, see [11], such that the symmetry*

$$\zeta(-p)=\zeta(p)-p\sigma_+,\qquad |p|<p^* \tag{4.1}$$

holds. More generally if $F_2,\ldots,F_n$ are any other $n-1$ functions of well defined parity under time reversal (i.e. even, $F_j(Ix)=F_j(x)$, or odd, $F_j(Ix)=-F_j(x)$) then setting $IF_j=F_j$ for F_j even and $IF_j=-F_j$ for F_j odd it is

$$\zeta(-p,If_2,\ldots,If_n)=\zeta(p,f_2,\ldots,f_n)-p\sigma_+ \tag{4.2}$$

The physical interpretation of $p\sigma_+$ as the average of the the thermostats entropy increase rate $\varepsilon_N=\frac{1}{N}\sum_{k=0}^{N-1}\frac{Q_j}{k_BT_j}$, makes the theorem of physical interest because, as mentioned, ε_N is a measurable quantity *independently of the model*.

The Eq.(4.2) is a special case of an even more general relation that is closely related to the Onsager-Machlup theory of *fluctuation patterns*, [12, 13, 14]. The question is which is the probability that the successive values of $F_j(S_t x)$ follow, for $t \in [-\tau, \tau]$, a preassigned sequence of values, that will be called *pattern* $\varphi(t)$, [8].

In a reversible hyperbolic and transitive system consider n observables $F_1, \ldots, F_n$ which have a well defined parity under time reversal $F_j(Ix) = \pm F_j(x)$. Given n functions $\varphi_j(t)$, $j = 1, \ldots, n$, defined for $t \in [-\frac{\tau}{2}, \frac{\tau}{2}]$ the question is: which is the probability that $F_j(S_t x) \sim \varphi_j(t)$ for $t \in [-\frac{\tau}{2}, \frac{\tau}{2}]$? The following,[8], gives an answer:

Fluctuation Patterns Theorem (FPT): *Under the assumptions of the fluctuation theorem given F_j, φ_j, and given $\varepsilon > 0$ and an interval $\Delta \subset (-p^*, p^*)$ the joint probabilities with respect to the SRB distribution that $F_j(S_t x)$ follows the pattern $\varphi_j(t)$ or the "time reversed pattern" $\pm\varphi_j(-t)$ (the sign depending on the parity of F_j) are related by*

$$\begin{aligned} &\frac{P_\mu(|F_j(S_t x) - \varphi_j(t)|_{j=1,\ldots,n} < \varepsilon, p \in \Delta)}{P_\mu(|F_j(S_t x) \mp \varphi_j(-t)|_{j=1,\ldots,n} < \varepsilon, -p \in \Delta)} = \\ &= \exp(\tau \max_{p\in\Delta} p\,\sigma_+ + O(1)) \end{aligned} \tag{4.3}$$

where sign choice $\mp$ is opposite to the parity of F_j and $p \stackrel{def}{=} \frac{1}{\tau}\int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{\sigma(S_t x)}{\sigma_+}\, dt$. The relation holds for patterns which can be realized with a probability that does not vanish faster than exponentially in time.

The FPT theorem means that "all that has to be done to change the time arrow is to change the sign of the entropy production", *i.e.* the *time reversed processes occur with equal likelyhood as the direct processes if conditioned to the opposite entropy creation.* This is made clearer by rewriting the Eq.(4.3) in terms of probabilities *conditioned on a preassigned value of* p; in fact up to $e^{O(1)}$ it becomes, [13], for $|p| < p^*$:

$$\frac{P_\mu(|F_j(S_t x) - \varphi_j(t)|_{j=1,\ldots,n} < \varepsilon,\, |\, p)}{P_\mu(|F_j(S_t x) \mp \varphi_j(-t)|_{j=1,\ldots,n} < \varepsilon,\, |\, -p)} = 1 \tag{4.4}$$

5 Consequences and comments

(i) In *stationary states* of reversible dynamics heat exchanges are constrained by (as remarked by Bonetto, [13, Eq.(9.10.4)]),

$$\langle e^{-\int_0^\tau \sum_j \frac{Q_j(t)}{k_B T_j}\, dt} \rangle = 1, \tag{5.1}$$

in the sense that $\frac{1}{\tau}\log\langle\cdot\rangle \xrightarrow[\tau\to\infty]{} 0$. Not to be confused with the formulae of [15] (and the later developments) dealing with properties either of equilibrium distributions or of distributions with density in phase space.

(ii) It should not be thought that p^* is proportional to the maximum of the finite time averages of $\varepsilon(S_t x)$. The value of p^* is the maximum value of p observable *with a probability which does not tend to zero faster than exponentially* as time tends to ∞, see [11]. This is analogous to the fact that in a hard sphere gas the close packing density is not the maximum of the density observable in finite volume.

(iii) it has been claimed that the CH is not necessary to prove FT: this is of course obvious. However some nontrivial assumption is necessary: the CH is a simple general property that captures the essential role of chaos, just as the harmonic oscillators systems capture the essence of the ordered motions.

(iv) The timed observations are closer to the physical applications than the observations in continuous time but it is, at least mathematically, interesting that the FT can be extended to continuous time observations, [16]. In physical applications, however, there may be an essential difference between the continuous version and the discrete one because sometimes the interaction potentials are modeled by forces which diverge at contact (e.g. when the interaction is of Lennard-Jones type) or in some special configurations. Then one cannot suppose that the system is Anosov because the spurious term $\dot{W}$ in the phase space contraction, Eq.(2.4), can become large with a probability that is "just exponentially small": and this will affect the fluctuation relation, [17]. The problem can be avoided by using timed observations: provided care is adopted in the choice of the timing events. One simply has to choose them so that the Poincaré section Σ does not contain the singular conficurations. In this way the contribution from the spurious terms, which has the form $\frac{1}{\tau}(W(\tau)-W(0))$, Eq.(2.7), will tend to zero as $t\to\infty$ and will be eliminated from the statistics of the entropy because W will be bounded at the times 0 and τ where it needs to be computed, [18, 17].

(v) In the checks of the fluctuation relation it is necessarily true that the time τ has to be kept finite: looking at the proof of the FT, [10, 11], the problem of the finite τ corrections, needed because the FT deals with an asymptotic property as $\tau\to\infty$, can be attacked and quantitatively studied, at least in some cases, [19], by following ideas employed to deal with "finite size effects" in statistical mechanics.

(vi) The extended form of the FT, Eq.(4.2), has been used to show that in the limit of 0 forcing the FT reduces to the ordinary fluctuation dissipation theorem, thus implying the Green-Kubo relations and Onsager reciprocity in reversible systems satisfying the CH, [20]. However assuming time reversibility only at 0-forcing and the CH it is sufficient to obtain the fluctuation-dissipation theorem, [21].

(vii) It has been claimed in the literature that the FT is a consequence of an analogous property of the equilibrium distributions: this is an erroneous claim, see [22] for a counterexample (which can be easily extended to cover even cases of very chaotic systems (a remark by F.Bonetto)). It is not possible to infer a property valid on the zero volume attractor from a property checked outside it.

(viii) It has been claimed that $\sigma_+ > 0$ is not necessary in the proof of FT: this is also not correct. It is essential not only because it appears in the denominator of the very definition of p but because positivity is used in the proof, see [11]. The error might be explained because the relation is written as a property of the not normalized $A = p\sigma_+$ *without conditions on the size of* A: which is very misleading because it deals with a quantity which could be 0 if $\sigma_+ = 0$. It is physically obvious that the relation FT holds for p in the domain of definition of ζ which is certainly finite under the CH, [11].

(ix) Since the chaotic hypothesis is never strictly speaking realized one refers to Eq.(4.1),(4.2) as a *fluctuation relation* (FR), and its test is a test of the chaotic hypothesis, in analogy with the tests of the ergodic hypothesis. So far there have been several studies of the FR via simulations. However there are only preliminary experimental results in experiments designed to check it in cases in which the system is not clearly modeled by equations on which a complete theory is also possible, [23]. A common feature to the attempts made so far to test the FR is that the function $\zeta(p)$ turns out to be not convex: a nice discussion of one of the reasons for this phenomenon can be found in [24].

(x) Perhaps the deepest consequence of the CH is the possibility of a precise theory of coarse graining: see [7] for a heuristic discussion from a Physicist viewpoint. The view stems out of the proof in [10, 11] of the FT and explains it, see also [25]. Furthermore the precise formulation of coarse graining leads to a discussion of the possibility of extending the notion of entropy to systems in steady non equilibrium, [26]. It also leads to an analysis of the irreversibility of processes and to a quantitative evaluation of their "degree of ireversibility", [27].

(xi) Reversibility is a delicate point: it might seem that it makes any check of the FR impossible, except in simulations. This is discussed in several places in the literature, see [28].

(xii) The CH is related, as mentioned, to the theory of turbulence. Conversely the analysis of the CH anf the fluctuation theorems has implications on the theory of turbulence, [29, 7, 14].

(xiii) The theory can be extended to quantum systems, [7], modeled by finite thermostats. Considering the system in Fig.1 let H be the operator on $L_2(\mathcal{C}_0^{3N_0})$, of symmetric or antisymmetric wave functions Ψ, $H = -\frac{\hbar^2}{2}\Delta_{\mathbf{X}_0} + U_0(\mathbf{X}_0) + \sum_{j>0}(U_{0j}(\mathbf{X}_0,\mathbf{X}_j) + U_j(\mathbf{X}_j) + K_j)$, parameterized by the configurations $(\mathbf{X}_j,\dot{\mathbf{X}}_j)_{j>0}$ of the particles in the thermostats (here $K_j \stackrel{def}{=} \frac{m}{2}\dot{\mathbf{X}}_j^2$) and consider the *classical* dynamical system on $(\Psi, (\{\mathbf{X}_j\}, \{\dot{\mathbf{X}}_j\})_{j>0})$:

$$\begin{aligned} -i\hbar\dot{\Psi}(\mathbf{X}_0) =& \ (H\Psi)(\mathbf{X}_0),\\ \ddot{\mathbf{X}}_j =& -\Big(\partial_j U_j(\mathbf{X}_j) + \langle\partial_j U_j(\mathbf{X}_0,\mathbf{X}_j)\rangle_\Psi\Big) - \alpha_j\dot{\mathbf{X}}_j \quad j>0 \end{aligned} \tag{5.2}$$

where the multipliers α_j are such to constrain the classical thermostats to have a constant kinetic energy $K_j = \frac{3}{2}N_j k_B T_j$

$$\begin{aligned} &\alpha_j \stackrel{def}{=} \frac{\langle W_j\rangle_\Psi - \dot{U}_j}{2K_j}, \qquad W_j \stackrel{def}{=} -\dot{\mathbf{X}}_j\cdot\partial_j U_{0j}(\mathbf{X}_0,\mathbf{X}_j)\\ &\sigma(\mathbf{X},\dot{\mathbf{X}}) \equiv \varepsilon(\mathbf{X},\dot{\mathbf{X}}) + \dot{W}(\mathbf{X}) \stackrel{def}{=} \sum_{j>0}\frac{Q_j}{k_B T_j} + \dot{W} \end{aligned} \tag{5.3}$$

which is time reversal symmetric if $I(\Psi,\mathbf{X},\dot{\mathbf{X}}) \stackrel{def}{=} (\overline{\Psi},\mathbf{X},-\dot{\mathbf{X}})$. If the CH is assumed the FT is expected to hold for this model, hence for the entropy creation rate, ε. See for more details [7].

Acknolwdgements: This paper was the text prepared for my talk at StatPhys23, given on the occasion of the Boltzmann medal ceremony. I wish to thank, in this occasion, *Daniela* (wife) and *Barbara* (daughter), my teachers to whom I owe what I understand and the way to look at Physics *Prof. Bruno Touschek, Prof.*

David Ruelle, Prof. Joel Lebowitz, Prof. EGD Cohen, my collaborators: from all I learnt far more than it might have appeared at times; in particular *Salvador Miracle-Solé, Giuseppe Benfatto* and more recently *Vieri Mastropietro, Guido Gentile, Federico Bonetto, Alessandro Giuliani*. It is a great honor to have been selected together with *Kurt Binder*. The actual lecture was somewhat different, due to time restrictions, and the transparencies can be found in the conference web-site, `http://www.statphys23.org`.

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