Fluctuation relation, fluctuation theorem, thermostats and entropy creation in non equilibrium statistical Physics

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A unified viewpoint is presented in margin to the "Work, dissipation and fluctuations in nonequilibrium physics" Bruxelles 22-25 March, 2006, where the topics were discussed by various authors and it became clear the need that the very different viewpoints be consistently presented by their proponents

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1. *Chaotic dynamics*

The *fluctuation relation* is a general symmetry property of mechanical systems which should hold under the only assumption that the system motions are *chaotic*: it reflects the *time reversal symmetry*.

Time reversal symmetry means a smooth isometry I of phase space which anticommutes with the time evolution map S_t: *i.e.* $IS_t = S_{-t}I$. Therefore the familiar operation of time reversal T or, even better, TCP would be always valid in fundamental models, [1], and therefore the time reversal symmetry can be an issue only if one deals with phenomenological models in which dissipation is empirically introduced: as in the case of Navier-Stokes equations for fluids, for instance.

The discovery, published in the paper [2], of the fluctuation relation has led to renewed efforts towards the formulation of a theory of nonequilibrium stationary states. In the paper a link is attempted with the earlier proposal [3] for the description of the probability distribution for chaotic stationary states in fluids. Although the paper was a real breakthrough, the original argument needed to be made precise. A direct connection with [3] was established and called "*fluctuation theorem*" in [4]: where it was shown how the paradigm of chaotic evolution constituted by the hyperbolic (also called "Anosov") systems allowed for a precise formulation of sufficient conditions under which the fluctuation relation held.

The latter proof has been considered interesting because in a sense the hyperbolic evolutions perform for chaotic systems the role plaid by the harmonic oscillators for ordered systems. From these works emerged the interest for Physics of two new fundamental concepts, the *chaotic hypothesis* and a general mechanical notion for the *entropy creation*.

The first is an extension of the proposals, [3], that identified the probability distributions forming the ensembles suitable to give the statistical properties of states of turbulent fluids with the special class of distributions, well known and studied in the theory of dynamical systems, called SRB distributions.

The extension can be formulated, [3, 4], in the form a hypothesis:

Chaotic Hypothesis: *Motion on the attracting set of a chaotic system can be regarded as "hyperbolic".*

This hypothesis is very ambitious as it should be seen as an extension of the *ergodic hypothesis*, which it implies if applied to a system which is isolated and subject only to conservative forces.

It allows us to state existence of time averages of mechanical observables $x \to F(x)$, identified with functions of the phase space point x representing the microscopic state of the system, *i.e.* the existence of the limits $\lim_{T\to\infty} \frac{1}{T}\sum_{j=0}^{T-1} F(S^j x)$ for all initial data x chosen in the vicinity of the attracting set, setting aside a set of 0 phase space volume. It also implies that, the limit is *independent* of x (apart from the zero volume possible exceptions) and therefore define a *statistics*, *i.e.* a probability distribution μ such that

$$\lim_{T\to\infty} \frac{1}{T}\sum_{j=0}^{T-1} F(S^j x) = \int \mu(dy)\, F(y) \qquad (1.1)$$

In other words for chaotic systems motions have a well defined statistics, *i.e.* a probability distribution that allows us to define (in principle) the time averages of the observables.

The nontriviality of the above statements becomes perhaps more clear in the case of systems subject to steady dissipation. Their stationary states cannot be described by statistics which are not *singular*: *i.e.* which attribute probability 1 to sets of 0 phase space volume.

This is a seemingly odd situation: we are interested in data randomly chosen with a probability distribution with density on phase space and, yet, they evolve with a statistics which is singular. Such a situation, however, appears to be quite clearly correct as soon as simulations are attempted in *virtually any* system which exhibits chaos (*i.e.* positive Lyapunov exponents) and is subject to some kind of dissipation: hence it is simply accounted for by the chaotic hypothesis, see for instance [5].

However technically the hypothesis is far more rich of implications. In fact the distribution μ is, in hyperbolic systems, identified with the SRB distribution, which is not well known but it should be viewed as a generalization of the microcanonical distribution for isolated systems. In a sense that can be made very precise it is the distribution that gives equal probability to cells into which the phase space can be imagined discretized, [6–8]. It allows to give a mathematical formula for the averages in (1.1) and even to give a precise definition of *coarse grained cells* in phase space, [6, 9, 10].

Without entering here in more technical details this means that we have, from the theory of the SRB distributions for hyperbolic systems, expressions for the averages in terms of mechanical quantities. The latter can therefore be used to derive general relations between observables averages *even though, as it is virtually always the case, we cannot hope to compute their actual vlaues.*

Just as in equilibrium where we can write the averages as integrals with respect to the Liouville distribution on the energy surface (or the canonical one) but we can hardly compute them: nevertheless we can establish, by using the formal expressions, general relations which turn out to be extremely interesting precisely because of their generality. A celebrated example is Boltzmann's *heat theorem*, *i.e.* the second law of equilibrium thermodynamics, as a consequence of the assumption that the statistics of motion (of an isolated system subject to conservative forces) is the microcanonical distribution.

The chaotic hypothesis has a rather general consequence which should be seen as a generalization, at any distance from equilibrium, of Onsager-Machlup fluctuations theory near equilibrium, [11, 12, 17].

Consider a mechanical system of particles described by a generic equation of motion for the representative point x in phase space

$$\dot{x} = f(x) \tag{1.2}$$

where x denotes the position and velocity components. The equation will be a model describing a finite system on which external non conservative forces act.

Therefore the equation will be non Hamiltonian and phase space volume will not be conserved. As a consequence the *divergence*

$$\sigma(x) = -\sum_i \partial_{x_i} f_i(x) \tag{1.3}$$

does not vanish. However in presence of time reversal symmetry it will be odd under time reversal $\sigma(x) = -\sigma(Ix)$. The system will be called *dissipative* if even the time average $\sigma_+ = \lim_{T\to\infty} \frac{1}{T}\int_0^T \sigma(S_t x)dt = \int \mu(dy)\sigma(y)$ of σ is *positive.*

In a dissipative system, $\sigma_+ > 0$, in the stationary state described by the statistics μ, consider the probability that $f_j(S_t x) \sim \varphi(t)$ for $t \in [-\frac12\tau, \frac12\tau]$ where $t \to \varphi(t)$ is a prescribed *pattern.* The symbol $\sim$ means that $|f(S_t x) - \varphi(t)| < \varepsilon$ for some very small ε (see [13–15] for a quantitative form of the notion of "very small"). Define the *dimensionless phase space contraction* $\sigma(x)$ as the divergence of the equations of motion changed in sign. Suppose that the average (with respect to the statistics μ, *i.e.* the integral of $\sigma(x)$ with respect to μ, see (1.1)) phase space contraction σ_+ is positive $\sigma_+ > 0$ and define $p = \frac{1}{T}\int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{\sigma(S_t x)}{\sigma_+} dt$. Suppose that $f_1(x), \ldots, f_n(x)$ are n observables with defined parity under time reversal, suppose odd for definiteness: $f_i(Ix) = -f_i(x)$. Then

Fluctuation relation *Suppose that the n observables form a complete set in the sense that the average phase space contraction p is determined by the patterns followed by the observables $f_1, \ldots, f_n$ (for instance σ is one among the f_j or p is the sum of the averages of some of the f_j). Then if $\sigma_+ > 0$ and the time evolution is reversible there exists $p^* \geq 1$ and*

$$\frac{P_\tau(\text{for all } j, \text{and}\, t \in [-\frac12\tau, \frac12\tau] \,:\, f_j(S_t x) \sim \varphi_j(t))}{P_\tau(\text{for all } j, \text{and}\, t \in [-\frac12\tau, \frac12\tau] \,:\, f_j(S_t x) \sim -\varphi_j(-t))} = \\ = e^{p\,\sigma_+\,\tau + O(1)}, \qquad |p| < p^* \tag{1.4}$$

where $P_\tau(E)$ denotes the probability of the event E with respect to the statistics SRB of the motions.

Remarks: (1) In particular this holds for the single observable $\sigma(x)/\sigma_+$, [4, 16], and *it is a theorem for hyperbolic systems.* This is the form in which the fluctuation relation was discovered, [2], and the above is an *extension* of it under the same assumptions, [13, 14].
(2) The extension was found first in the special case $f_1 = \sigma(x)/\sigma_+, f_2 = \partial_E \sigma(x)$ where it has been shown to imply the Onsager reciprocity and Green-Kubo formulae, [17].
(3) Another particular case is obtained by considering the probability that the averages $\overline{f}_1, \ldots, \overline{f}_n$, over the time interval $(-\frac{\tau}{2}, \frac{\tau}{2})$ of the considered observables, have a given value $a_1, \ldots, a_n$ with p determined by $a_1, \ldots, a_n$. Then for $|p| < p^*$

$$\frac{P(\overline{f}_1 \sim a_1, \ldots, \overline{f}_n \sim a_n)}{P(\overline{f}_1 \sim -a_1, \ldots, \overline{f}_n \sim -a_n)} = e^{p\sigma_+\tau + O(1)} \tag{1.5}$$

which is a very surprising relation because of the arbitrariness of the observables f_j *which do not appear in the r.h.s.* except through their function p. The above relation appeared recently in the context of Kraichnan's theory of passive scalars in a case in which $p = \sum_i a_i$, [18].
(4) A mahematically precise form of the theorem, [4, 19], is to say that for $|p| < p^*$ the probability that $p \in \Delta$ has the form $\exp(\tau \max_{p\in\Delta} \zeta(p) + O(1))$ and the function $\zeta(p)$, which for hyperbolic systems is known to be analytic and convex in a natural interval of definition $(-p^*, p^*)$ (and $-\infty$ outside it) satisfies, for $|p| < p^*$ the symmetry property

$$\zeta(-p) = \zeta(p) - p\sigma_+ \tag{1.6}$$

(5) A further consequence is that the stationary average of $\exp\int_0^\tau \sigma(S_t x)dt$ satisfies

$$\langle e^{\int_0^\tau \sigma(S_t x)dt}\rangle \sim 1 \tag{1.7}$$

where ~ 1 means that the quantity is *bounded* as $\tau \to \infty$ (*Bonetto*'s formula, [14, Eq.(9.10.4)]): see below for a hint to possible applications and for its similarity to Jarzynski's formula, [20, 21].
(6) The chaotic hypothesis and the fluctuation relation have been tested quite extensively, starting with [5], and it has almost become a test of the correctness of the computer programs simulations of chaotic systems rather than a formula to be tested. The situation is quite different with experiments where a lot of difficulties arise, on a case by case basis, in setting up experiments and interpreting them. Nevertheless there have been several attempts and it can be hoped that more will come, [22–27].
(7) The formulae above hold for time evolutions described by maps iterations as well as for those described by differential equations. It is worth stressing that most works, in particular [4], deal with discrete time evolutions. The case of continuous time is considered less frequently, and for the first time it has been formulated as a theorem in [16]. The case of maps is possibly closer to applications as observations are usually done when some timing events occurr and evolution appears as a map between timing events. However a close examination of the relations between the continuous and discrete cases reveals a number of delicate properties (particularly in the case in which singular forces may be acting, like Lennard-Jones type of repulsive cores) which if neglected may lead to errors, as exemplified in [28].

2. *Entropy creation*

The result in the previous section hints at another major point of the research in the last 20 years of the '900's: in the '980's a concrete model of a thermostat became necessary to perform simulations of molecular dynamics in systems out of equilibrium.

The "Nosé–Hoover", the "isokinetic" or the "isoenergetic" thermostats are prominent examples that were put forward and employed to study a large number of problems: see [29] for a thorough discussion of the related problems. One of the results was the discovery of the flutuation relation.

Another important byproduct was the identification of the (not yet defined at the time) *entropy creation rate* with the phase space contraction. Although the original authors quite clearly attributed to the words they employed a meaning close to the physical one suggested by the given names the general attitude was, it seems, to regard the thermostat models as unphysical and, consequently, to attribute little value to the concept of entropy creation as related in some way to the thermodynamic entropy.

The above (extension) of the fluctuation theorem and relation, (1.4), suggests that one should give a *fundamental physical sense to the phase space contraction*, at least in finite, time reversible systems. Since as said above ultimately time reversal (or the equivalent, for our purposes, TCP symmetry) is a law of nature all models should either display the symmetry or be equivalent to symmetric models.

In my view this identification between phase space contraction and entropy creation rate is an important new development, [29–31], that is still not fully appreciated as it should.

It has to be stressed that, although since more than a century we are familiar with the entropy of equilibria and its mechanical interpretation, no mechanical definition of entropy creation rate in a process out of equilibrium has been proposed (or, better, accepted). The above extended fluctuation relation is clearly saying that the independence of the ratio in (1.5) means that the conditional probability that a pattern occurs in presence of an average (dimensionless) phase space contraction p is the same as that of the reverse pattern in presence of the opposite average phase space contraction (*i.e.* $-p$).

In other words if the entropy creation rate is reversed during a time interval then evolution of the *other* observables "proceeds backwards" with the same likelyhood it had to "proceed forward" when the average entropy production was p. *All that has to be done to reverse the time arrow is the reverse the entropy creation rate.*

All this leads to say that the identification of entropy creation rate and phase space contraction has to be taken seriously. Its identity with what one would naturally call entropy creation in the many particular cases studied in the works summarized in [29] and continuing since should not be considered a curious coincidence but as a new insight into the foundations of nonequilibrium statistical mechanics.

Note that we are saying that in nonequilibrium entropy creation is defined and identified with mechanical quantities: but entropy itself is not defined (yet?), not even in stationary states. It might even be not needed and not unambiguous, [9, 14].

To illustrate further the new identification of entropy creation rate with the mechanical quantity expressed by the divergence of the equations of motion, (1.3), and its physical interest I discuss a class of examples which, it seems to me, fully justify the mentioned identification, [32, 33].

Consider a mechanical system $\mathcal{C}_0$ in contact with the mechanical systems $\mathcal{C}_i$, $i = 1, 2, \ldots$. Microscopically the state is is described by the positions $\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$ of the $N_1, N_1, \ldots, N_n$ constituent particles. The systems interact via short range pair forces with potential energies $U_a(\mathbf{X}_i)$, $U_a(\mathbf{X_i}, \mathbf{X_0})$. There is no direct interaction between the particles in $\mathcal{C}_a$, $a > 0$.

The systems in $\mathcal{C}_a$, $a > 0$ should be thought as "thermostats" acting on the system $\mathcal{C}_0$ across the separating walls via their mutual pair interactions.

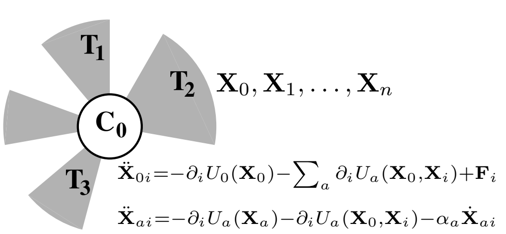

Fig.1: Schematic illustration of the geometry. The equations of motion are written here assuming unit mass for the particles.

The thermostats *temperature* T_a is defined to be proportional to the kinetic energy via the Boltzmann's constant k_B. Setting $K_a \equiv \frac{1}{2}\sum_a \dot{\mathbf{X}}_a^2 \stackrel{def}{=} \frac{3}{2}k_B T_a N_a$, it is supposed constant and kept such by the action of suitable (phenomenological) forces on the i-th particle in $\mathcal{C}_a$ of the form $-\alpha_a\dot{\mathbf{X}}_{ai}$. The α_a can be taken

$$\alpha_a = \frac{W_a - \dot{U}_a}{3N_a k_B T_a} \tag{2.1}$$

where where the work performed by the system on the thermostats particles $-\sum \dot{\mathbf{X}}_a \cdot \boldsymbol{\partial}_{\mathbf{X}_a} U_a(\mathbf{X}_0, \mathbf{X}_a)$ can be called $W_a = \dot{Q}_a =$ heat given to the thermostat $\mathcal{C}_a$ by the system in $\mathcal{C}_0$. The external forces $\mathbf{F}_i$ are assumed to be purely positional.

Given the above dynamical model (for heat transport) remark that it is *reversible* and time reversal is just the usual velocity reversal (because the thermostat forces are *even* under global velocities change). Furthermore the divergence of the total phase space volume can be immediately computed and turns out to be $\sigma(\mathbf{X}) = \sigma_0(\mathbf{X}) + \dot{U}(\mathbf{X})$ with

$$\sigma_0(\mathbf{X}) = \sum_{a=1}^{n} \frac{\dot{Q}_a}{k_B T_a}\,\frac{3N_a - 1}{3N_a} = \sum_{a=1}^{n} \frac{\dot{Q}_a}{k_B T_a} \tag{2.2}$$

where $U(\mathbf{X}) = \sum_{a=1}^{n} \frac{U_a}{k_B T_a}\,\frac{3N_a-1}{3N_a}$, and $O(N_a^{-1})$ has been neglected in the last equality in (2.2).

When computing time averages the "extra term" $\dot{U}$ will not contribute because being a time derivative its average will be $\frac{1}{T}(U(S_T\mathbf{X}) - U(\mathbf{X}))$ and therefore will give a vanishing contribution for large T and the average of $\sum_{a=1}^{n} \frac{\dot{Q}_a}{k_B T_a} = \sigma_0$ will be the average of σ. If the interaction U is bounded also the fluctuations of the averages of σ and σ_0 will coincide. In the cases in which the interactions are not bounded (*e.g.* Lennard-Jones repulsive cores) care has to be exercised in the fluctuations analysis: the picture does not change except in a rather well understood, trivial, way and this will not be discussed here, [28, 34].

Note that σ_0 is a "boundary term", in the sense that it depends on the forces through the boundaries and the forces are supposed short range. Thus the question arises whether such kind of thermostats and short range interactions can lead to stationary states: this is not obvious but the "efficiency" of such thermostats has been investigated in molecular dynamics simulations, [35, 36], leading (not surpringly) to the result that the thermostat mechanism in Fig.1 can lead to stationary states (even in presence of additional positional forces stirring the particles in $\mathcal{C}_0$).

Since the thermotats are regarded in equilibrium the above expression shows that $\sigma(\mathbf{X})$ can be "legitimately" called the entropy increase of the reservoirs: so the mechanical notion of phase space contraction acquires a clear physical meaning: and this is a no small achievement of a long series of works based on simulations of molecular dynamics, [29, 31].

3. *Comments*

(1) Other studies of fluctuations have been proposed: they are rather different and apply to systems which are not stationary. The object of study are initial data *sampled within an equilibrium distribution* of a Hamiltonian system and subsequently evolved with the equations of motion of a dissipative time reversible system.

Then the phase space contraction averaged over a time τ, $a \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau \sigma(S_t x)dt$, will be such that the probability $P_0(a)$ *with respect to the initial equilibrium distribution* for a to have a given value is such that

$$\frac{P_0(a)}{P_0(-a)} = e^{a\tau}. \tag{3.1}$$

This is an exact identity, immediately following from the definitions. It involves *no error terms*, unlike the "similar" (1.6) that can be written also as $\frac{P(p)}{P(-p)} = e^{p\sigma_+\tau+O(1)}$, with P the *probability with respect to the stationary distribution*, which is *singular* with respect to the equilibrium distributions if $\sigma_+ > 0$.

It has been claimed that, being valid for all times, it implies the fluctuation relation, (1.6), for stationary states (at least when the stationary state exists). This would imply a simple, direct and *assumptionless* derivation of the fluctuation theorem in (1.7) and should hold in spite of the fact that in [4] an assumption about the chaotic nature of the motions is needed to derive it, together with a rather detailed understanding of the nature of chaotic systems.

However a derivation of the fluctuation theorem (1.6) from (3.1) involves considering (3.1) *after* the limit $\tau \to \infty$ has been performed: a rather unclear procedure (note that the *r.h.s.* depends on τ). Leaving aside the logical consitency problems it should be kept in mind that in the stationary state, at least in the interesting cases in which $\sigma_+ > 0$ and there is dissipation, the statistics of motion will be controlled by a distribution that has nothing to do with the initial equilibrium distribution in which the averages in (3.1) are considered.

Therefore the claim is incorrect and it is no surprise that some kind of chaos has to be present to obtain the fluctuation relation (1.6). In fact one can give examples of simple systems in which (3.1) holds for all times, the system evolves towards a stationary state and nevertheless the (1.6) *does not hold*, [37]. The confusion has crept into the literature and even affected experiments: this can only be explained by a certain lack of attention to the literature due to the urge to find an easy way of testing the large fluctuations in real systems (fluids, granular materials, or even biological systems).

Another aspect of (3.1) is that it involves a rather than $p = a/\sigma_+$. This is clearly a matter of convention: however care has to be exercised because the fluctuation relation (1.6) is valid for $|p| < p^*$ with $p^* \geq 1$ being a physically nontrivial quantity, [19]. In terms of a this means that it is valid for $|a| < \sigma_+$. Overlooking this fact has led to think that it should hold for all a's and has led to errors in the literature. The errors are particularly noticeable in cases in which σ_+ is close to zero, when the interpretation of simulations becomes quite difficult because long time scales become relevant. It has to be noted that σ_+^{-1} is a time scale diverging as $\sigma_+ \to 0$, see the discussion in [28].

(2) A different, interesting, fluctuation result is *Jarzynski's formula* which provides the means of computing the free energy difference between two *equilibrium states* at the same temperature.

Imagine to extract samples $x = (p, q)$ in phase space with a canonical probability distribution $\mu_0(dpdq) = Z_0^{-1} e^{-\beta H_0(p,q)} dpdq$, with Z_0 being the canonical partition function, and let $S_{0,t}(p, q)$ be the solution of the Hamiltonian *time dependent* equations $\dot{p} = -\partial_q H(p, q, t), \dot{q} = \partial_p H(p, q, t)$ for $0 \leq t \leq 1$. Let $H_1(p, q) \stackrel{def}{=} H(p, q, 1)$, then, [20, 21],

Consider the "time 1 map" $(p', q') \stackrel{def}{=} S_{0,1}(p, q)$ *and call* $W(p', q') \stackrel{def}{=} H_1(p', q') - H_0(p, q)$ *the corresponding variation of the energy function. Then the distribution* $Z_1^{-1} e^{-\beta H_1(p',q')} dp'dq'$ *is exactly equal to the distribution* $\frac{Z_0}{Z_1} e^{-\beta W(p',q')} \mu_0(dpdq)$. *Hence*

$$\langle e^{-\beta W} \rangle_{\mu_0} = \frac{Z_1}{Z_0} = e^{-\beta \Delta F(\beta)} \tag{3.2}$$

where the average is with respect to the Gibbs distribution μ_0 *and* ΔF *is the free energy variation between the equilibrium states with Hamiltonians* H_1 *and* H_0 *respectively.*

Remark: (i) The reader will recognize in this *exact identity* an instance of the Monte Carlo method. Its interest lies in the fact that it can be implemented *without actually knowing* neither H_0 nor H_1 nor the *protocol* $H(p, q, t)$. To evaluate the difference in free energy bewteen two equilibrium states *at the same temperature* of a system that one can construct in a laboratory, when the system changes its energy function from H_0 to H_1 (not necessarily explicitly known), then "all one has to do" is
(a) To fix a protocol, *i.e.* a procedure, to transform the forces acting on the system along a well defined *fixed once and for all* path from the initial values to the final values in a fixed time interval ($t = 1$ in some units), and
(b) Measure the energy variation W generated by the machines implementing the protocol. This is a really measurable quantity at least when W can be interpreted as the work done on the system, or related to it.
(c) Then average of the exponential of $-\beta W$ with respect to a large number of repetition of the protocol abd apply (3.2). This can be useful even, and perhaps mainly, in biological experiments.
(ii) Imagine a protocol consisting in lifting a container with a gas in equilibrium to height z: the Hamiltonian changes by Mgz, if M is the total mass and g gravity constant. Eq. (3.2) of course is correct, being an identity, and gives a free energy variation equal to βMgz while normally one would say that the free energy, and every other thermodynamic quantity, should have remained unchanged. Whether or not there has been a free energy variation really depends on what one is interested in studying. Thus if the interest is in measuring free energy variations in a biology experiment care has to be given (and is actually given) to make sure that the protocol followed does not introduce spurious, quite hidden, forms of work. This makes, once more, clear that the application of a mathematical identity to real systems requires careful examination of the conclusions drawn.

The two formulae (3.2) and (1.7) bear some similarities but are, however, quite different:

(1) the $\int_0^\tau \sigma(S_t x)\, dt$ in (1.7) is an entropy creation rather than the energy variation W.

(2) the average in (1.7) is over the SRB distribution of a stationary state, in general out of equilibrium, rather than on a canonical equilibrium state.

(3) the (1.7) says that $\langle e^{-\int_0^\tau \varepsilon(S_t x)\, dt} \rangle_{SRB}$ is bounded as $\tau \to \infty$ rather than being 1 exactly unlike (3.2) which holds without corrections, [20, 21].

The (3.2) has proved useful in various equilibrium problems (to evaluate the free energy variation when an equilibrium state with Hamiltonian H_0 is compared to one with Hamiltonian H_1); hence it has some interest to investigate whether (1.7) can have some consequences.

If a system is in a steady state and produces entropy at rate σ_+ (*e.g.* a living organism feeding on a background) the fluctuation relation (1.6) and its consequence Bonetto's formula, (1.7), gives us informations on the fluctuations of entropy production, *i.e.* of heat produced, and (1.7) *could be useful*, for instance, to check that all relevant heat transfers have been properly taken into account. This suggests that the fluctuation relation for stationary states could have some applications even in experiments in biology and be a valuable complement to (3.2).

(3) Finally the identification of entropy creation and pase space contraction suggests a possible quantitative measure for "how irreversible" is a transformation be-

tween two different stationary states (equilibrium or not). Since physical processes are often accompanied by volume changes with time $V \to V_t$ it is natural to allow them and to change the definition of phase space contraction (2.2) to, [33],

$$\sigma^\Gamma(\mathbf{X}) = \sigma_0(\mathbf{X}) + \dot{U} - N\frac{\dot{V}_t}{V_t} \tag{3.3}$$

where N is the number of particles in the volume V.

Then one can try to define the "irreversibility time scale" $\tau(\Pi)$ for a process Π measuring the time scale over which the process manifests its irreversibility. Suppose that in the process Π the parameters controlling the forces change with time from an initial value $\mathbf{F}_0$ to a final one $\mathbf{F}_\infty$; to be definite suppose

$$\mathbf{F}(t) = \mathbf{F}_0 + (1 - e^{-\gamma t})(\mathbf{F}_\infty - \mathbf{F}_0) \tag{3.4}$$

The (3.4) allows us to consider the *quasi instantaneous* changes ($\gamma \to \infty$) as well as the *quasi static* ones ($\gamma \to 0$).

Starting the N–particles system in the stationary state μ_0 with parameters $\mathbf{F}_0$ it evolves to μ_t and, eventually, to the stationary state μ_∞ with parameters $\mathbf{F}_\infty$.

Let $\mu_{srb,t}$ = be the SRB distribution with parameters $\mathbf{F}(t)$ "frozen" at value taken at time t. Then if σ_t^{srb} is the entropy creation rate in the "frozen" state $\mu_{srb,t}$ an *irreversibility time scale* for Π could be defined as

$$\tau(\Pi)^{-1} = \frac{1}{N^2}\int_0^\infty \Big(\langle\sigma_t^\Gamma\rangle_{\mu_t} - \langle\sigma_t^{srb}\rangle_{SRB,t}\Big)^2 dt \tag{3.5}$$

which can be checked to give the "expected results" in simple cases like the Joule expansion, see [33]. Quasi instantaneous processes Π have a short $\tau(\Gamma)$, meaning that irreversibility becomes noticeable immediately, while quasi static processes have a long $\tau(\Pi)$ indicating the opposite situation.

(4) Although the above analysis is restricted to particle systems it can be extended to more general systems, in particular to fluids and turbulence. Not surprisingly as turbulence has been a source of inspiration for the development of the above ideas, [15, 33].

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REVTEX

[1] G. Gallavotti, Physica D **112**, 250 (1998).
[2] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Physical Review Letters **71**, 2401 (1993).
[3] D. Ruelle, Annals of the New York Academy of Sciences **357**, 1 (1980).
[4] G. Gallavotti and E. G. D. Cohen, Physical Review Letters **74**, 2694 (1995).
[5] F. Bonetto, G. Gallavotti, and P. Garrido, Physica D **105**, 226 (1997).
[6] G. Gallavotti, Journal of Statistical Physics **78**, 1571 (1995).
[7] G. Gallavotti, Lecture Notes in Physics, ed. Garrido–Marro **448**, 271 (1995).
[8] G. Gallavotti, Open Systems and Information Dynamics **6**, 101 (1999).
[9] G. Gallavotti, Communication in Mathematical Physics **224**, 107 (2001).
[10] G. Gallavotti, cond-mat/0606477 (2006).
[11] L. Onsager and S. Machlup, Physical Review **91**, 1505 (1953).
[12] L. Onsager and S. Machlup, Physical Review **91**, 1512 (1953).
[13] G. Gallavotti, chao-dyn/9703007, in Annales de l' Institut H. Poincaré **70**, 429 (1999).
[14] G. Gallavotti, *Statistical Mechanics. A short treatise* (Springer Verlag, Berlin, 2000).
[15] G. Gallavotti, *Foundations of Fluid Dynamics* ((second printing) Springer Verlag, Berlin, 2005).
[16] G. Gentile, Forum Mathematicum **10**, 89 (1998).
[17] G. Gallavotti, Physical Review Letters **77**, 4334 (1996).
[18] R. Chetrite, J. Y. Delannoy, and K.Gawedzki (2006).
[19] G. Gallavotti, Mathematical Physics Electronic Journal (MPEJ) **1**, 1 (1995).
[20] C. Jarzynski, Physical Review Letters **78**, 2690 (1997).
[21] C. Jarzynski, Journal of Statistical Physics **98**, 77 (1999).
[22] R. Van Zon and E. G. D. Cohen, Physical Review Letters **91**, 110601 (+4) (2003).
[23] K. Feitosa and N. Menon, Physical Review Letters **92**, 164301+4 (2004).
[24] R. V. Zon, S. Ciliberto, and E. Cohen, Physical Review Letters **92**, 130601 (+4) (2004).
[25] N. Garnier and S. Ciliberto, Physical Review Letters **71**, 060101 (+4) (2005).
[26] S. Ciliberto, N. Garnier, S. Hernandez, C. Lacpatia, J. Pinton, and G. R. Chavarria, Physica A pp. 240–250 (2004).
[27] M. Bandi, J. R. Cressman, and W. Goldburg, nlin.CD/0607037 (2006).
[28] F. Bonetto, G. Gallavotti, A. Giuliani, and F. Zamponi, Journal of Statistical Physics **123**, 39 (2006).
[29] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Fluids* (Academic Press, New-York, 1990).
[30] D. Ruelle, Communications in Mathematical Physics **189**, 365 (1997).
[31] D. Ruelle, Journal of Statistical Physics **95**, 393 (1999).
[32] G. Gallavotti, Journal of Statistical Physics **84**, 899 (1996).
[33] G. Gallavotti, Chaos **16**, 023130 (+7) (2006).
[34] R. V. Zon and E. G. D. Cohen, Physical Review E **69**, 056121 (+14) (2004).
[35] G. Ayton, E. Evans, and D. Searles, Journal of Chemical Physics **115**, 2033 (2001).
[36] P. Garrido and G. Gallavotti, cond-mat/0607231 and mp_arc 06-197 (2006).
[37] E. G. D. Cohen and G. Gallavotti, Journal of Statistical Physics **96**, 1343 (1999).