Nonequilibrium thermodynamics ?

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Twentyseven comments (•) on the Second Law and nonequilibrium systems

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I. DEFINITIONS.

The purpose, in the present discussion, is investigating the possibility of an extension of Thermodynamics to systems which are in a stationary state but are subject to the action of conservative and nonconservative positional forces $\underline{f}_{pos}$ and (therefore) also to the action of the forces $\underline{\vartheta}$ necessary to take away the heat thus generated.

We first consider systems for which a finite microscopic mechanical model exists and are, therefore, described by equations of the form

$$m\,\underline{\ddot{x}} = \underline{f}_{pos}(\underline{x}) + \underline{\vartheta}(\underline{x},\underline{\dot{x}}) \stackrel{def}{=} \underline{F}(\underline{x},\underline{\dot{x}})$$

and $\underline{x}$ is a point in an appropriate finite dimensional phase space (typically of very large dimension). If the force $\underline{f}_{pos}$ is conservative then no thermostat is needed and we suppose $\underline{\vartheta} = \underline{0}$ (for simplicity). In general we call the force law $\underline{\vartheta}$ a *mechanical thermostat*.

(•) A key notion will be the *phase space contraction rate* $\sigma(\underline{\dot{x}},\underline{x})$ which is defined as minus the divergence of the equations of motion:

$$\sigma(\underline{\dot{x}},\underline{x}) = -\sum_{\alpha=1}^{3N} \partial_{\dot{x}_\alpha} F_\alpha(\underline{\dot{x}},\underline{x})$$

(•) An equilibrium state will be a stationary probability distribution given by a density (one says a stationary "*absolutely continuous*" distribution) on the phase space of a system which is subject only to conservative forces. We also identify the distribution with any point which is typical with respect to it: by typical we mean that the time averages of observables evaluated on the trajectory of the point are the same as the averages with respect to the distribution.

(•) We suppose (ergodicity) that the time averages of observables (just of the *few* physically relevant for macroscopic Physics) are computable from any of the (equivalent) statistical ensembles: like the microcanonical ensemble. Hence an equilibrium state is identified with a probability distribution on phase space. A "typical" microscopic configuration, *i.e.* an initial datum in phase space which is not in a set of "unlucky cases" which, however, form a zero volume set and are therefore (believed to be)[1] unobservable, will evolve in time so that the time averages of the observables (at least the *few* relevant for macroscopic Physics) are computable by the equilibrium state which has the correct values of the macroscopic parameters: *e.g.* in the microcanonical case the energy U and the container volume V. When we speak of properties of a single (typical) point in phase space, like of its "entropy", we always mean the same property of the equilibrium state for which the datum is a typical one.

Remarks: This already might be controversial: in fact the above (admittedly unconventional) definition of entropy has the following implications. A rarefied gas which initially happens to have all molecules located in the left half of a container, because a separation wall has just been removed, setting the gas in macroscopic motion and out of the previous equilibrium state, will be an initial datum in phase space whose entropy is that of the same gas occupying the entire container and at the same temperature[2] (the difference residing only in the different dynamics that follows the removal the wall in the middle of the container). Since a physicist would apply the Boltzmann equation to describe the evolution, the question arises about which is the place here of Boltzmann's H function, which is different if evaluated for the initial datum or for a datum into which the initial one evolves after a moderately large time (and in both cases it equals the classical thermodynamic entropy of the initial and final equilibria).

(•) In trying to study nonequilibrium cases a conceptual difficulty must be met: if a system is subject to external non conservative forces then the thermostatting forces will have a non zero divergence and volume in phase space will not be preserved. The key idea (due to Ruelle)[1] is that in this case (as well as in the previous case) the nonequilibrium states will be the stationary states which are generated by time averaging of initial states that have a density or more satisfactorily, perhaps, by time averaging on the evolution of initial data that are typical

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1 This is not to be taken for granted, even though it is very often considered so: here I do not enter into discussing this mysterious assumption (as I have nothing to say).

2 Assuming the gas to be ideal: we think here of Joule's experiment. In the following the temperature will have the dimension of energy, *i.e.* we call temperature T what is usually called $k_B T$ with k_B being Boltzmann's constant

for probability distributions given by some (arbitrary) density. The latter states are called *SRB distributions* (Sinai,Ruelle,Bowen)[1–4]. Their appearance is natural since there will be *no state* (*i.e.* no probability distribution) which is stationary and at the same time is also given by a density. As in the equilibrium state we shall attribute to each individual point in phase space the macroscopic properties of the stationary state which allows us to compute the averages of macroscopic observables on the motion of the given point.

Remark: Systems that are chaotic in a mathematical sense (*hyperbolic systems*) can be shown, on rather general grounds, to have the property that there is only one SRB distribution (with the correct values of the macroscopic parameters).[1,2,4] Therefore such systems, the only ones for which the above definition has a strict mathematical sharpness, verify an extension of the ergodic hypothesis: adopting the latter definition means believing that the system is *chaotic enough* so that typical initial data generate a unique stationary distribution with several features of the SRB distributions for hyperbolic systems: the assumption has been called *chaotic hypothesis*[5] and it represents (in our analysis) the nonequilibrium analogue of the classical ergodic hypothesis.

(•) Given an initial state (a typical point or a distribution on phase space) it might be possible to define a function of it that will monotonically increase to a limit value which is the same for almost all data sampled with a distribution with a density on phase space (*i.e.* absolutely continuous). Since Boltzmann's H function is an example of such a function we shall call H-functions all such functions. We recall that Boltzmann's H function is defined by a coarse graining of phase space into "macrostates" determined by the occupation numbers $f(p,q)d^3pd^3q$ of phase space cells d^3pd^3q around p,q and by defining $H = -\int f(p,q)\log f(p,q)\, d^3pd^3q$. Clearly here the cells size affects by an additive constant the actual value of H, which therefore should have no significance (at least in the classical mechanics context in which we are working) and only the variations of H can be meaningful. In a rarefied gas the Boltzmann equation is believed to apply:[3] so that in the latter cases the function just defined is a nontrivial example of an H–function.

(•) Here we propose that even in the case of rarefied gases it is neither necessary nor useful that the H function is *identified with the entropy*: we want to consider it as a Lyapunov function whose role is to indicate which will be the final equilibrium state of an initial datum in phase space. This does not change, nor it affects, the importance of Boltzmann's discovery that, in rarefied gases, the H function can be identified with the physical entropy whenever the latter is defined (*i.e.* in equilibria). Suppose that the initial state is chosen randomly with respect to a Gibbs distribution which is *not* the one that pertains to the given parameters that describe the system (*e.g.* volume V and energy U) but to other values: for instance it is chosen randomly with a Gibbs distribution $\mu_{U,V/2}$ that has the same energy but occupies half of the volume as in Joule's experiment. Then the inital and final values of the H function happen to coincide with the physical entropies of the Gibbs states $\mu_{U,V}$ and $\mu_{U,V/2}$ (at least in a rarefied gas) which are given by the Gibbs' entropy.[3]

(•) The latter property could possibly be used to attempt a definition of entropy for states which are neither equilibrium nor stationary states:[6] however such a definition would be useful only in the special situations in which an H-theorem could be proved. That seems effectively to reduce the cases in which the notion would be useful to the ones in which an initial equilibrium state identified by some parameters (like U, V) evolves towards a final one identified by other values of the parameters. And even in such cases it is severely restricted to the rarefied gases evolutions in which the H-theorem can be proved: a statement that a model indpendent, universal, extension of the above H-function, would have to be proved to have a monotonicity property, at least at a heuristic level, to avoid that its monotonicity becomes an *a priori* law of nature.

(•) In general I would think that there will always be a Lyapunov function which describes the evolution of an initial state and is maximal on the stationary state that its evolution will eventually reach: however such a Lyapunov function may not have a universal form (unlike the H function in the rarefied gases cases) and it may depend on the particular way the system is driven by the external forces. After all the SRB distribution verifies a variational principle (Ruelle)[1,2,4] which *remarkably* has the same form both in equilibrium and nonequilirium systems and one may imagine that in general it will be possible to define (on a case by case basis, I am afraid) a quantity that will tend to a maximum reached on the eventual stationary state. This picture seems to me simpler than trying to guess a (possibly nonexistent) general

[3] One should note that in the whole Boltzmann's work he has been really concerned with the approach to equilibrium: in our terminology he has been concerned with the problem of determining the stationary equilibrium distribution to which a given initial datum gives rise at large time: restricting consideration only to such cases one could well call the Boltzmann's H-function the "entropy" of the state as it evolves towards equilibrium. And, whatever name we give it, remains true that H is a measure of the disorder in the system. Our analysis here is intended to say that such an interpretation is not tenable when the system evolves towards a stationary nonequilibrium state. It must also to be said that even the H-theorem is *not general* because it applies only to rarefied gases, and even there it is an approximation: to generalize it to general situations, even when one only deals with approach to equilibrium, is a profound statement which should be substantiated by appropriate arguments.

definition of a quantity that would play the role of Boltzmann's H.

II. ENTROPY CREATION.

The second law of Thermodynamics, in classical Thermodynamic treatises, states:

It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from a cooler to a hotter body

Of course this will be assumed to be a law of nature (Clausius)[7].

(•) The law implies that one can define an *entropy* function S on all equilibrium states of a given system (characterized in simple bodies by energy U and available volume V) and if an equilibrium state 1 can be transformed into another equilibrium state 2 then

$$S_2 - S_1 \ge \int_1^2 \frac{đQ}{T}$$

using notations familiar from Thermodynamics: here the integral is over the transformation followed by the system in going from 1 to 2 and the $đQ$ is the heat that the system absorbs at temperature T from the outside reservoirs with which it happens to be in contact. The equality sign holds if the path followed is a reversible one.

(•) One should note that the principle really says that the $\int_1^2 \frac{đQ}{T}$ does not depend on the path followed, if the path is a reversible sequence of equilibrium states; and its maximum value is reached along such paths. Existence of a path connecting 1 with 2 with $S_2 - S_1 < \int_1^2 \frac{đQ}{T}$ would lead to a violation of the second law.

(•) Is there an extension of the $S_2 - S_1 \ge \int_1^2 \frac{đQ}{T}$ relation to nonequilibrium Thermodynamics?[4] Since there seems to be no agreement on the definition of entropy of a system which is in a stationary nonequilibrium and since there seems to be no necessity in Physics of such a notion, at least I see none, I shall *not* define entropy of stationary nonequilibrium systems (in fact the analysis that follows indicates that if one really insisted in defining it then its natural value could, perhaps, be $-\infty$!).

(•) In Thermodynamics one interprets $-\int_1^2 \frac{đQ}{T}$ as the *entropy creation* in the process leading from 1 to 2, *be it reversible or not or through intermediate stationary states or not.* The name is chosen because it is thought as the entropy increase of the heat reservoirs with which the system is in contact and which are supposed to be systems in thermal equilibrium: so that their entropy variations are, in principle, well defined because they fall in the domain of equilibrium thermodynamics. In a general transformation from a state 1 to a state 2, both of which are stationary (non)equilibrium states, following a path of (non)equilibrium stationary states $\mu^{(t)}$ and in contact with purely mechanical thermostats one could consider the contribution to the *entropy creation* due to irreversibility in the process leading from 1 to 2 during a time interval $[0, \Theta]$ to be

$$\Delta = c \int_0^\Theta \langle \sigma(\underline{x}\,,\,\dot{\underline{x}}) \rangle_{\mu^{(t)}} dt = c \int_0^\Theta \sigma_t \, dt$$

where $\sigma_t \stackrel{def}{=} \langle \sigma(\underline{x}\,,\,\dot{\underline{x}}) \rangle_{\mu^{(t)}}$ is the average phase space contraction computed in the state $\mu^{(t)}$. This follows a recently proposed identification of $\sigma(\underline{x}\,,\,\dot{\underline{x}})$ as proportional to the *entropy creation rate* (here c is a proportionality constant)[8]. The quantity Δ is for mechanical thermostats the analogue of $-\int_1^2 \frac{đQ}{T}$ for the generic phenomenological thermostats characterized by a temperature T.

(•) In considering macroscopic systems one may imagine situations in which a system is partially thermostatted by mechanical forces for which a model considered physically reasonable is available[5] and partially by phenomenologically defined "heat reservoirs" characterized by a temperature T and able to cede to the system quantities $đQ$ of heat ($đQ$ can have either sign or vanish).

In such more general settings a system in contact with several thermostats of which a few are modeled by mechanical equations and a few others are unspecified and are just assumed to exchange quantities of heat $đQ$ at temperature T the second principle will be extended as

$$-\Delta + \int_1^2 \frac{đQ}{T} \le 0$$

assuming that the path leading from 1 *to* 2 *consists entirely of nonequilibrium stationary states* and that it lasts a time interval $[0, \Theta]$. Regarding the external thermostats as thermodynamic equilibrium systems $-\frac{đQ}{T}$ is the entropy increase of the reservoirs at temperature T and $\Delta = c \int \langle \sigma \rangle_t$ is interpreted as the entropy increase of the mechanical reservoir: if this interpretaton is accepted the above relation becomes the ordinary second law for the external reservoirs and could be read as "the entropy

[4] Which in a sense is tantamount of asking "is there a nonequilibrium Thermodynamics?"

[5] Typically these are models of friction, as in the Navier Stokes equation case in which the viscosity plays the role of a thermostat. Or in granular matter where the restitution coefficient in the collisions produces energy dissipation. Another well known example is in Drude's theory of electrical conduction.

of the rest of the universe does not decrease" (because $\Delta - \int_1^2 \frac{d\!\!/ Q}{T} \ge 0$), where "universe" is not the astronomical Universe but rather the collection of physical systems whose interaction with the system under study cannot be neglected.

If a system is a in a stationary state in which $\sigma_t = \langle\sigma\rangle > 0$ (t–independent) this essentially forces us to say that its entropy, if one insisted in defining it at the time t_0 of observation, could only be $-\int_{-\infty}^{t_0} \langle\sigma\rangle\, dt = -\infty$ as hinted above.[6]

(•) Since the quantity σ_t is ≥ 0 (Ruelle)[2] under very general conditions (in fact always if the chaotic hypothesis is assumed to hold true) $\Delta \ge 0$ and the proposed estension is compatible with the main consequences of the second law. The constant c will be taken 1 because the factor 1 can be computed by studying the expression of $\sigma(\underline{x}, \dot{\underline{x}})$ in special models: at the moment, however, I see no immediate physical implications of the "universality" of this choice of c and for the purposes of what follows c could be any constant, even non universal.

(•) The above implies again that we shall *not* be able to define an entropy function *unless* $\sigma_t \equiv 0$. The latter is the condition under which equilibrium Thermodynamics is set up: so that if one studies only transformations from equilibrium states to other equilibrium states it is possible to define not only the creation of entropy but the entropy itself (up to an additive constant).

(•) A number of compatibility questions arise: suppose that the system evolves between 1 and 2 under the action of a thermostat which is modeled by forces that act on the system. For instance we can imagine a container with periodic bounday conditions, we call it a *wire*, containing a lattice of obstacles, which we call a *crystal*, and N particles, which we call *electrons*, interacting between each other and with the lattice via hard core interactions (say) and subject also to a constant force, which we call *electromotive force*, of intensity E; furthermore the particles will be subject to a thermostat force of Gaussian type[7] (as it is essentially the case in Drude's theory as described in classical electromagnetism treatises[9]) which forces the particles to have an energy $U = u(E)$ which is an assigned function of E. Suppose that the value of E changes in time (very slowly compared to the microscopic time scales) following a profile $E(t)$ as drawn in Fig.1

$E(t)$

Fig.1

Θ

In this case the wire performs a cycle which is irreversible and the integral $\int_1^2 \frac{d\!\!/ Q}{T}$ is 0 because the system is adiabatically isolated (the thermostat being only of mechanical nature). The entropy variation of the system is defined because the initial and final state are equilibria and, since they are the same, it is 0: but there has been entropy creation $\Delta > 0$.

(•) *It is* (perhaps) *natural to define the "temperature" of a mechanical thermostat* by remarking that in the models studied in the literature it turns out that σ_t is proportional to the work per unit time that the mechanical forces perform, the porportionality constant being in general a function of the point in phase space. Therefore we can call T_0^{-1} the time average of the proportionality constant between σ and the work W per unit time that the mechanical thermostatting forces perform: in this way $\sigma_t = \frac{W}{T_0}$ and $\int_0^\Theta \sigma_t\, dt = \int \frac{d\!\!/ Q_0}{T_0}$ where $\oint Q_0$ is the total work performed by the mechanical forces *which we can* (naturally) *call the heat absorbed by the mechanical reservoir.*

(•) If one imagines that the above conducting wire model at the same time exchanges heat with two sources, absorbing Q_2 at temperature T_2 and ceding Q_1 at temperature T_1 via some unspecified mechanism, and assuming that the profile of $E(t)$ is as in Fig.2

$E(t)$

E_0

Fig.2

Θ

where the value of E_0 corresponds to a temperature T_0 in the above sense. The inequality $-\Delta + \int_1^2 \frac{d\!\!/ Q}{T} \le 0$ becomes

$$-\int_0^\Theta \sigma_t\, dt + \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \equiv -\frac{Q_0}{T_0} + \frac{Q_2}{T_2} - \frac{Q_1}{T_1} \le 0$$

For instance, we see that if $T_1 = T_2 = T_0$ we have realized a cycle which is irreversible. In it a quantity of heat $Q_2 - Q_1 - L$, with $L = Q_0 = T_0\Delta = T_0 \int_0^\Theta \sigma_t\, dt$ is absorbed at a single temperature $T = T_0$ and is transformed into the amount $Q_2 - Q_1 - L$ of work: however the inequality forbids this to be positive, as expected.

III. MECHANICAL AND STOCHASTIC MODELS.

A definition in Physics is interesting (only) if it is useful to decribe properties of the systems in which we are interested. Therefore having set the above definitions one should expect to be asked why all the work was made.

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[6] If we imagine possible to replace a mechanical thermostat with a phenomenological thermostat at temperature T then the left hand side of the relation above remains unchanged but a part of $-\Delta$ becomes a contribution to the second addend.

[7] This is not the appropriate place to remind the Gauss' least constraint principle: it can be easily found in the literature[3].

In this case the whole matter was originated by efforts to interpret results that started to appear in the late 1970's concerning numerical experiments in molecular dynamics[8].

(•) It is obvious that in numerical experiments one needs to deal with a finite system (and even not too large): hence various models of thermostats were devised for the purpose of obtaining equations that could be transformed into numerical codes and studied on electronic machines. This was a theoretical innovation with respect to previous models which either relied on stochastic boundary conditions or, in the more sophisticated cases, with (poorly understood) systems with infinitely many particles. And it opened the way to import the knowledge in the theory of dynamical systems that had been being developed in the two preceding decades or so.

The novelty with respect to stochastic thermostats was more conceptual than numerical. Given the number of particles a stochastic code is often only mildly more complex (and it could even be simpler) at least in the cases in which the noise is uncorrelated in time and acts on one particle at a time. This means that the resulting code does not require a longer running time than a deterministic one: a fact that can also be seen by noting that a stochastic system can be regarded as a deterministic system with more degrees of freedom (*i.e.* the ones needed to describe the random numbers generators that one has to use and which, as it is well known, are simply suitably chaotic dynamical systems themselves).

From the point of view of code writing this amounts at adding a few more particles to the system.[8]

(•) It is by no means clear that by using mechanical thermostats one can obtain physically realistic models nor, assuming that the stochastic dynamic models are more realistic, models behaving in as complex a way as the stochastic ones (typically consisting in boundary collision laws in which the particles emerge with a maxwellian velocity distribution with suitable variance, *i.e.* suitable temperature). Understandably the matter is controversial but quite a few researchers think that this has been positively demonstrated by large amounts of work done in the last thirty years.

Since stochastic models are just models with more degrees of freedom it is tautological that there is equivalence between all possible stochastic models and all deterministic ones. The real question is whether the rather simple deterministic thermostats models that have been used are able to simulate accurately the stochastic models believed to be more realistic.

(•) In my view it is likely that vast classes of thermostats, deterministic and stochastic as well, are equivalent in the sense that they produce motions which although very different when compared at equal initial conditions and at each time have, nevertheless, the same statistical properties[3,4]. And in my opinion there is already evidence that it is indeed possible to simulate the same system with simple deterministic thermostats or with some corresponding stochastic ones.

Here the equivalence is intended in a sense that is familiar in the theory of equilibrium ensembles: if one fixes suitably certain parameters then ensembles (*i.e.* time invariant probability distributions in phase space) that are apparently very different (*e.g.* microcanonical and canonical) give, nevertheless, the same statistical properties to vast (*not all*) classes of observables. If one fixes the energy U and the volume V in a microcanonical ensemble or the inverse temperature β and the volume V in the canonical ensemble then one obtains that local observables have the same statistical distribution in the two cases provided the value of β is chosen such that the average canonical energy is precisely U.

One among the most striking examples of such equivalence (She,Jackson)[10] is the equivalence between the dissipative Navier Stokes fluid and the Euler fluid in which the energy content of each shell of wave numbers is fixed (via Gauss' least constraint principle) to be equal to the value that Kolmogorov's theory predicts to be the energy content of each shell at a given (large) Reynolds number. Here one compares two very different mechanical thermostats. A more general view on the equivalence between different thermostats has been developed since. In fact many instances in which Physicists say that "an approximation is reasonable" really correspond to equivalence statements about certain properties of different theories (and in the best cases the statements can be translated into proper mathematical conjectures).

(•) Coming therefore to consider more closely mechanical thermostat models the phase space contraction has turned out in many cases to be an interesting quantity often intepretable as the ratio between the work done by the thermostats on the systems and some kinetic energy average: this led since the beginning to identify the phase space contraction rate with the entropy creation rate. The above "philosophical" considerations have been developed to give some background interpretation to the vast phenomenology generated by the new electronic machines used as tools to investigate complex systems evolutions.

A collision between the previously held views, egregiously summarized by the book of De Groot-Mazur[11], based on *continuum mechanics* and the new approaches based on *transistors, chips and dynamical systems theory* ensued: often showing that the two communities give the impression of not really meditating on each other arguments.

[8] For instance if the stochastic thermostat is defined by requiring that upon collision with the boundary a particle rebounds with a maxwellian velocity distribution with dispersion (temperature) depending only on the boundary point hit then one needs three Gaussian random number generators, *i.e.* essentially three more degrees of freedom.

(•) Setting aside controversies it is interesting that the mechanical thermostats approach has nevertheless led to a new perspective and to a few new results. Here I mention the *fluctuation relation*: the phase space contraction $\sigma(x(t),\dot{x}(t))$ which in various models has interesting physical meaning (like being related to conductivity or viscosity) is a fluctuating quantity as time goes on. Its average value in a time interval of size τ divided by its infinite time average in the future $\langle\sigma\rangle$ is a quantity p that still fluctuates. Of course it fluctuates less and less the larger is τ and its probability distribution (easily analyzable by observing it for a long time and by dividing the time into intervals of size τ and forming a histogram of the values thus observed) is expected on rather general grounds to be proportional to $e^{\tau\zeta(p)}$ for τ large with $\zeta(p)$ being a function with a maximum at $p=1$ (*i.e.* at the average, hence most probable, value of p) *provided* $\langle\sigma\rangle>0$, *i.e.* provided there is dissipation in the system and the system is, therefore, out of equilibrium.

If the dynamical equations are *reversible*, *i.e.* if there is an isometry I of phase space which anticommutes with the time evolution $(x,\dot{x})\to S_t(x,\dot{x})\equiv(x(t),\dot{x}(t))$ in the sense that $IS_t=S_{-t}I$ and furthermore $I^2=1$ then, provided the system motion is "very chaotic", it follows that

$$\zeta(-p)=\zeta(p)-p\langle\sigma\rangle$$

This is a *parameter free* symmetry relation that was discovered in a numerical experiment (Evans, Cohen, Morriss)[12] and which has been checked in many cases. By very chaotic one means that the motion of the system can be assimilated to that of a suitable Anosov flow whose trajectories fill densely phase space (transitive Anosov flow).

(•) Indeed for transitive reversible Anosov systems the above relation holds as a theorem[5]. Since models of physical systems are *not* Anosov systems from a strict mathematical point of view the above relation cannot be applied, not even to cases in which the model is reversible and the trajectories are dense on the allowed phase space: the chaotic hypothesis says that the fact that the system is not mathematically an Anosov system is not relevant for physical observations, in most cases. This is similar to the statement that in equilibrium systems the lack of ergodicity of motions is irrelevant in most cases and averages can be computed by assuming ergodicity (*i.e.* by using the microcanonical distribution).

If this is correct the above relation should hold: a non trivial fact to check due to the difficulty of observing such large fluctuations *and* to the lack of free parameters to fit the data, once they have been laboriously obtained.

(•) When the forcing of the system is let to 0 the above relation degenerates: not only $\langle\sigma\rangle\to0$ but also p itself becomes ill defined as its definition involves division by $\langle\sigma\rangle$. Nevertheless by extracting the leading behavior of both sides the fluctuation relation leads to relations between average values of derivatives of dynamical quantities with respect to the intensity of the forcing, *evaluated at zero forcing*, and such relations can be intepreted as Onsager reciprocity relations and Green–Kubo expressions for suitably defined transport coefficients[4].

(•) Clearly a reversibility assumption on thermostats is a strong assumption and so is the chaotic hypothesis. Nevertheless the results are interesting and they seem to be among the few that can be obtained in a field which is well known for its imperviousness. The philosophical framework developed in Sections 1,2 helps keeping a unified view on a subject that is being developed although, strictly speaking, one could dispense with the philosophical view and concentrate on obtaining results that can be drily stated without appealing to entropy, entropy creation, thermostats *etc.*

(•) And one can go beyond various assumptions via the use of equivalence conjectures between different thermotats: for instance Drude's thermostat model which strictly speaking is not reversible is conjectured to be equivalent to a Gaussian thermostat which is reversible. The Navier Stokes equation for incompressible fluids, clearly irreversible, is conjectured to be equivalent to a similar reversible equation[4] as the quoted experiment[10] shows and as other successive experiments seem to confirm[13]. The research along the just mentioned lines seems to go quite far and to lead not only to new perspectives but also to new results or confirmations (*i.e.* non contradictions) of the general views in Sections 1,2. Doubts about the whole approach can be legitimately raised, and have been raised, on the grounds that the results are too few and too meager to be really interesting: for instance one can hold against their consideration that they are not even sufficient to give some hint at a derivation of "elementary" relations like Fourier's law or Ohm's law. One can only say that time is not yet ripe to see whether the new methods and ideas lead really anywhere or at least to a better understanding of some of the problems that also the old ones have not been able to tackle, so far, (like the heat conduction laws or the electric conduction laws) in spite of intense research efforts.

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[1] Ruelle D. *Turbulence, strange attractors and chaos*. World Scientific, New-York, 1995.

[2] Ruelle D. Smooth dynamics and new theoretical ideas in non-equilibrium statistical mechanics. *Journal of Statistical Physics*, 95:393–468, 1999.

[3] Gallavotti G. *Statistical Mechanics. A short treatise*. Springer Verlag, Berlin, 2000.

[4] Gallavotti G. *Foundations of Fluid Dynamics*. Springer Verlag, Berlin, 2002.

[5] Gallavotti G. and Cohen E.G.D. Dynamical ensembles in nonequilibrium statistical mechanics. *Physical Review Letters*, 74:2694–2697, 1995.

[6] Lebowitz J. Boltzmann's entropy and time's arrow. *Physics Today*, September:32–38, 1993.

[7] Zemansky M.W. *Heat and thermodynamics*. McGraw-Hill, New-York, 1957.

[8] Evans D.J. and Morriss G.P. *Statistical Mechanics of Nonequilibrium Fluids*. Academic Press, New-York, 1990.

[9] Becker R. *Electromagnetic fields and interactions*. Blaisdell, New-York, 1964.

[10] She Z.S. and Jackson E. Constrained euler system for navier-stokes turbulence. *Physical Review Letters*, 70:1255–1258, 1993.

[11] de Groot S. and Mazur P. *Non equilibrium thermodynamics*. Dover, 1984 (reprinted).

[12] Evans D.J., Cohen E.G.D., and Morriss G. :. Probability of second law violations in shearing steady flows. *Physical Review Letters*, 70:2401–2404, 1993.

[13] Gallavotti G., Rondoni L., and Segre E. Lyapunov spectra and nonequilibrium ensembles equivalence in 2d fluid mechanics. *Submitted*, pages 1–20, 2002.