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A conference on nonequilibrium thermodynamics.

G. Gallavotti

Rutgers Hill Center, I.N.F.N. Roma1, Fisica Roma1

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Abstract

In transformations involving stationary nonequilibria entropy might be a not well defined concept. It might be analogous to the heat content (once called "caloric") in transformations that are not isochoric (*i.e.* which involve mechanical work): it could be just a quantity that can be transferred or created, like heat in equilibrium. The text summarizes the philosophy behind a recently proposed definition of entropy creation in nonequilibrium stationary systems.

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I. Thermostats and chaotic hypothesis.

In studying equilibrium and nonequilibrium thermodynamics the notion of *thermostat* plays an important role: it is usually defined empirically [1] as a physical system capable only of exchanging heat without changing temperature or performing work (hence it is ideally an infinite system). One can also envisage concrete mechanisms to keep a system in a stationary state, realized by a mechanical force of nonconservative nature.

Here I want to consider mechanical systems which, in spite of being acted upon by nonconservative forces, are kept in a stationary state by other mechanical forces, and to study which relations, if any, can be established between the various stationary states, [2]. The transformations between the stationary states will be "*quasi static*" trasformations through intermediate stationary states.

I shall consider only systems consisting of many particles and I shall *not* consider systems that are modeled by continua (the latter can be regarded as an idealization in which several many particles systems are put together, *one per "volume element"*, and studied on time and space scales vastly different from the ones we consider for the evolution of the simple systems which we imagine to constitute the volume elements of the continuum, [3]). Continua can be considered but one first must understand the thermodynamics of a simple system, [3].

The particle motions occurring in a simple system are assumed to be chaotic: the *chaotic hypothesis*, [4], essentially states that an isolated system of particles has chaotic evolution on the microscopic time scales, *i.e.* on the time scale of mean free flight.

A simple system will be described by a differential equation in its phase space: we write it as $\dot{x} = X_E(x)$ where $x = (\,\dot{\underline{q}}\,,\,\underline{q}\,) \in R^{6N} \equiv \Omega$ (*phase space*), N=number of particles, m= mass of the particles, with

$$m\,\ddot{\underline{q}} = f(\,\underline{q}\,) + \underline{E}\,\cdot\,\underline{g}\,(\,\underline{q}\,) - \vartheta_{\underline{E}}\,(\,\dot{\underline{q}}\,,\,\underline{q}\,) \equiv X_E(x)$$

where $f(\,\underline{q}\,)$ describes the internal (conservative) forces (*e.g.* hard cores), $\underline{E}\cdot\underline{g}\,(\,\underline{q}\,)$ represents the "external forces" (nonconservative) acting on the system: for definiteness we suppose that they are locally conservative (like an electromotive force) but not globally such, and $\underline{\vartheta}_{\,\underline{E}}$ is the force law which models the action exerted by the thermostat on the system to keep it from indefinitely acquiring energy: this is why we shall call it a *mechanical thermostat.* Linearity of the dependence on the "fields" $\underline{E}$ is only for convenience: we are *not* assuming them to be small (the theory of linear nonequilibrium is amply discussed in the literature, [5]); at any rate we know, since Onsager, that what is really relevant is an intrinsic duality between forces and fluxes and the parameterization of the forces induces a corresponding definition of the fluxes, see below. More generally the external forces could be velocity dependent and even time dependent (periodically) and we restrict to positional forces for simplicity.

Assumption (chaotic hypothesis, [4])*: The system evolution is assumed as chaotic as possible, i.e. the it is assumed to be hyperbolic (one also says, technically, that the system is "an Anosov system").*

Models of thermostats in the above sense can be very different even for the same macroscopic system; for instance (a list far from exhaustive)

(1) assuming the system to have hard cores one can suppose that the collisions are inelastic: the head-on component of the energy is decreased by a scale factor $\eta < 1$ upon each collision or, *alterntively*, the total energy of the two colliding particles is rescaled and assigned a given value $3k_BT$ ("Drude's condution model"), [6], or

(2) assuming that there is a background friction $\vartheta_i = -\nu\dot{q}_i$, $\nu > 0$, for all components of $\ddot{x}_j$ or

(3) assuming *minimum effort* to keep, say, the total kinetic energy or the total energy constant, ("*Gaussian thermostat*", [7]).

Stochastic thermostats could also be allowed (they just add degrees of freedom to the equations) but we do not consider them here.

II. SRB statistics and nonequilibrium ensembles

Any initial state x, randomly chosen in phase space with a probability distribution which has a density in phase space (in jargon "absolutely continuous distribution with respect to Liouville measure"), *will admit a statistics* (under the above chaotic assumption): *i.e.* for all (smooth) observables F

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T F(S_t x)dt = \int_\Omega \mu_E(dy)F(y)$$

where $\mu_{\underline{E}}$ is a stationary probability distribution on phase space, called the *SRB distribution* or *SRB statistics*,[3,8–10] .

Definition: A system in a microscopic state x which has SRB statistics $\mu_{\underline{E}}$ is said to be in the stationary state $\mu_{\underline{E}}$. The collection of all stationary states of a system that are constructed by varying the parameters (typically the volume V of the container, the particles number N, the external forces $\underline{E}$, etc) will be called a "nonequilibrium ensemble".

Hence here an *ensemble* is a collection of probability distributions but, often, terminology indicates an ensemble to be *a single element* of the collection: with such an understanding what would be here called simply the "microcanonical ensemble" would become "the collection of the microcanonical ensembles": this being in my view too awkward I have adopted calling an ensemble already the whole collection of distributions (as the french word ensemble literally suggests).

The notion of nonequilibrium ensemble is wider than in equilibrium as it depends *also* on the equations of motion, hence on the thermostat model. Therefore one expects that, as it happens in equilibrium statistical mechanics, there should be "equivalent ensembles" corresponding to classes of different possible models for thermostats acting on a system, [3,9].

Equilibrium is a special case of nonequilibrium: in such case $\underline{E} = \underline{0}$ and $\underline{\vartheta}_{\underline{E}} = \underline{0}$ and the chaotic hypothesis implies the validity of the ergodic hypothesis and the family of SRB distributions can be parameterized by total energy U and volume V and coincides with the microcanonical ensemble, [9].

We now want to consider which relations can be established in general between the properties of stationary states that can be transformed into one another by changing the external parameters.

If we limit ourselves to equilibrium states then it is well known since Boltzmann (in his papers in the period 1866–1884, see [11]) that if a transformation generates an energy variation dU and a volume variation dV when the pressure (defined microscopically) is p and the average kinetic energy is $\frac{3}{2}Nk_BT$ then, [9],

$$\frac{dU + p\,dV}{T} = \text{exact}$$

while $dU + p\,dV$ is not exact, *except* in the isochoric case (*i.e.* when $dV = 0$) and it is called the *heat transferred* from the reservoirs to the system. It makes no sense to talk of amount of heat contained in the system unless one limits oneself to isochoric transformations: there is no *caloric* (*i.e.* no *heat content*) unless one allows only the latter type of transformations in which the system performs no work (and in that case it is just another name for internal energy).

Defining *entropy* as a primitive of the exact differential $(dU + p\,dV)/T$, the immediate question is whether one can extend the notion of *entropy* content to non equilibrium states.

III. Entropy creation rate and temperature.

The proposal that emerges from certain theoretical considerations and a number of numerical experiments (I share here the view of a few people who put it forward), [7,9,12,13], is to define, if k_B is Boltzmann's constant,

Definition: The entropy creation rate s *in a stationary state* $\mu_{\underline{E}}$ *is* $s = k_B \sigma$ *with*

$$\sigma = \int_\Omega \mu_{\underline{E}}(dx)\sigma(x)$$

where $\sigma(x) = -$ *divergence of* $\underline{X}_{\underline{E}}(x)$ *and* $\mu_{\underline{E}}$ *is the SRB statistics.*

An important general theorem,[14], guarantees that $\sigma \ge 0$, and $\sigma = 0$ corresponds to the case in which the SRB distribution $\mu_{\underline{E}}$ admits a density on phase space, a case that one naturally identifies with an equilibrium state and which essentially happens only if $\underline{E} = \underline{0}$.

The above definition leads to a natural definition of temperature of the thermostatting forces: note that there is no universally accepted definition of temperature in systems out of equilibrium, even if stationary, [2,15]. Namely one sets

Definition: the temperature T *of the thermostats for a stationary nonequilibrium state is*

$$T = \frac{W}{s}$$

where W *is the work per unit time done on the system by the external forces and* s *is the entropy creation rate.*

The idea of relating the notion of temperature to the entropy creation rate stems from a connection between temperature and the fluctuation theorem (see below) pointed out by F. Bonetto inspired by the connection between the definition of temperature, the failure of the fluctuation dissipation relation at non zero forcing, [16], and the fluctuation theorem.

The above definition does not make sense as such in equilibrium because it becomes 0/0: however one can imagine introducing a small forcing and a corresponding thermostat. Then in the limit of vanishing forcing this yields a definition of T which by the "fluctuation dissipation theorem" would be correct, [16–18].

Adopting the above concepts leads naturally to giving up the possibility of defining entropy content of a system: in nonequilibrium thermodynamics entropy ends up to be undefined and one can speak only of "entropy creation" or "transfer": much as "caloric" or "heat content" is undefined in equilibrium thermodynamics. Should one insist in defining the entropy content of a dissipating (*i.e.* with $\sigma > 0$) stationary state one would be compelled to assign to it a value $-\infty$, because the system creates entropy at a constant rate.

IV. Cycles.

A few tests can be performed on the above notions, [2]. For instance imagine that a system performs a cycle from stationary state 1 to stationary state 2 identical to 1 except for the time of its realization through intermediate stationary states, for instance by switching on and off an external field E, see figure 1.

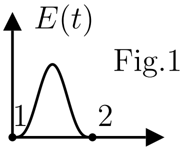

Fig.1

In this case we expect that an observer who knows nothing about the microscopic features of the thermostats will see work performed by the system in a cycle and he would expect a corresponding release of heat, by energy considerations: and the heat emitted has to be related to the temperature in such a way that the entropy increase of the thermostats is ≥ 0: this is the case if entropy creation is defined as above because $\oint_1^2 \sigma_\tau d\tau \ge 0$.

One can also imagine mixed situations in which heat is partially (*i.e.* during part of the transformation) absorbed by one or more phenomenological heat reservoirs and partly (*i.e.* in the complementary part of the transformation) by a detailed, mechanically modeled, action on the system.

In this situation (not envisaged in equilibrium thermodynamics where only phenomenological thermostats are considered), see figure 2,

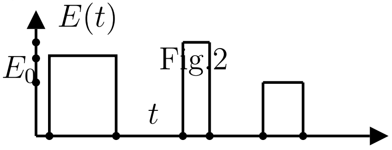

Fig.2

the second law would be consistently extended to say that

$$k_B \oint_1^2 \sigma_\tau d\tau + \oint_1^2 \frac{dQ}{T} \ge 0$$

if dQ is the amount of heat ceded to the reservoir at temperature T. This implies that even by using mechanical thermostats one cannot produce work in cycles by only interacting with reservoirs at the same temperature, [2].

V. H-functions.

The above is not in contradiction with the possibility of existence of a function which, given an initial state x, will evolve monotonically until reaching a maximum value, the same for almost all x in phase space, [19,20]: and this is not in contrast with microscopic reversibility. For instance in the case of the evolution of a rarefied gas we can imagine to divide the one particle phase space into cells C, "of appropriately chosen size $|C|$", [19], and call $f_C(x)$ the occupation number of each cell by the particles in x. Then, if $t \to S_t x$ denotes the time evolution of the initial data x at time t,

$$-k_B \frac{1}{t} \int_0^t \sum_C f_C(S_\tau x) \log f_C(S_\tau x)\, dt$$

will converge, and for practical purposes monotonically after a short transient, as $t \to \infty$ to a limit which, if the Boltzmann equation holds within a good approximation, maximizes $-k_B \sum_C p_C \log p_C$, $p_C \ge 0$, (subject to the conservation constraints like $\sum_C p_C = N$, *e.t.c.*, [19]) and the limit value is given by the entropy S of the equilibrium state associated with x. If Boltzmann's equation is (unreasonably) dismissed then still the above quantity will converge to essentially the same limit but the time average will be important as the integrand will not "practically converge" to S but it will show very rare large fluctuations which, however, are doomed to occur at time intervals larger than the age of the Universe, *i.e.* do not occur at all for "all" purposes (I suppose that the number of particles of the system is large, say $> 10^3$): neglecting such impossible events would in fact dispense from considering the time average in the above limit relation. However it is not clear that there should be a universal definition of such "*Lyapunov functions*" or "*H–functions.* I think that they can certainly be defined on a case by case basis but not necessarily in a general universal way: for instance in fluids of higher density in the last formula one should use the Resibois H–function, [21]; and this is so, I think, essentially because it is not possible to define an entropy content for non equilibrium states: which is the quantity that would naturally play the role of a universal H–function.

Note however that other views are possible if entropy and heat are conceptually separated: and recently a quite general and universal definition has been proposed identifying the H–function with the logarithm of the volume occupied in phase space by the phase space points which are macroscopically indistinguishable ("defining the same *macrostate*"): this applies when the notion of macrostate is free of ambiguities (or is at least possible), and it is certainly an interesting proposal which has already received support from numerical experiments, [20]. The value S of this quantity could be a possible definition of entropy of the stationary state that is eventually achieved by the evolution of all phase space points that correspond to the same macrostate. Although S would possibly be unrelated to the amounts of heat that are transferred in the transformations between stationary states, calling it "entropy" would be justified on the basis of its coincidence with entropy in the case of equilibrium states and of its nature as a Lyapunov function for the approach to stationarity.

VI. Remarks.

(1) The above analysis, if accepted, allows us to define entropy as a notion related to heat axchanges only for the stationary states which are in the very special class of equilibrium states. It is important to mention one more study that has been made in the attempt of defining entropy as a function of nonequilibrium stationary states.

One can consider an evolution of a phase point under forces which up to time t_1 are constant and admit a stationary SRB distribution μ^1, then the forces vary between t_1 and t_2 and become again constant after time t_2. If one *fixed* the forces $\underline{E}\,(t)$ at their value at any $t \in [t_1, t_2]$ then the dynamics would admit a SRB distribution. Therefore we can define for each t the stationary SRB distribution $\overline{\mu}_t$ corresponding to the "frozen" forces $\underline{E}\,(t)$ and, at the same time, the (different) probability distribution μ_t into which μ^1 evolves in the time interval $[t^1, t]$, and we can also define $\sigma(\tau) = \int \sigma_\tau(x)\mu_\tau(dx)$ and $\overline{\sigma}_\tau = \int \sigma_\tau(x)\overline{\mu}_\tau(dx)$.

Then a quantity which is possibly of interest is

$$I = k_B \int_{t_1}^{t_2} (\sigma(t) - \overline{\sigma}_t)\, dt$$

This is a quantity that does not really depend on how long a time the system dwells on a special value of the parameters since the integrand will go to zero fast if the interval is too long (because μ_t will approach $\overline{\mu}_t$).

Does I depend on the intermediate stationary states of the transformation? Some aspects of the question have been partially studied, [22], and I interpret them as *suggesting* that to first order in the variation of the force parameters (during the intermediate times) independence might hold (I stress that this is a conjecture). More precisely: if the variation of the forces vanishes rapidly at $t_2 = +\infty$, hence the evolving distribution μ_t returns to μ^1 and the system performs a cycle then the value of I does not depend on the actual intermediate pattern of the variation of the forces, *to first order in the variations.* However the same work suggests that very likely this is no longer true already to second order: going in the direction of making difficult attempts at defining entropy variations in stationary nonequilibria on the basis of the quantity I..

(2) Having defined the notion of entropy creation rate one can define a "duality" between fluxes J_j and forces E_j using $\sigma(x)$ as a "generating function":

$$J_j(\underline{E}) = k_B \frac{\partial \sigma}{\partial E_j}$$

which, at $\underline{E} = \underline{0}$, leads to Onsager's reciprocity and to Green–Kubo's formulae for transport, [17,18].

(3) We have proposed a definition of entropy creation rate and of temperature for a class of stationary states. But a new definition is really useful if it is associated with new results: I think that such new results may already be around and cluster around the *fluctuation theorem*, but for this I refer to the literature, [2,4,15,23–26].

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e-mail `gallavotti@roma1.infn.it`
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