Quantum Nonequilibrium and Entropy Creation

Giovanni Gallavotti
Fisica and I.N.F.N. Roma 1
13 Jan 2007

Abstract: *In sharp contrast to the corresponding classical systems cases it is not yet understood how to define a mechanical quantity with the interpretation of entropy creation rate for nonequilibrum stationary states of finite quantum systems with finite thermostats. Some aspects of this problem are discussed here in cases in which identifying entropy creation rate as a mechanical observable might be possible.*

1. Classical systems and thermostats

The aim of this paper is to propose a notion of thermostat acting *reversibly* on a quantum mechanical system which is analogous to the Gaussian or Nosé-Hoover thermostats that have been so important in recent times for the development of research non nonequilibrium. At the same time we remark that "entropy creation" can be associated with the thermostats discussed here and can be given a meaning that makes it susceptible of experimental measurements. This is important also because it allow us to extend the "chaotic hypothesis" to such systems and to test the "fluctuation relation" that holds, at least as a formal consequence. I begin by recalling the notion of classical thermostat that will be genreralized here and some results concerning classical nonequilibrium statistical mechanics.

A *thermostat* is, physically, a device that extracts heat created inside a mechanical system subject to non conservative forces, thus allowing control of the energy build-up: in this way a forced system can reach a *stationary state*. Such a state is however deeply different from an equilibrium state. Heat, matter or electric currents may be present and the dissipation associated with the thermostats implies that the probability distribution μ that describes the statistical properties of the system is not even close to the familiar Maxwell-Boltzmann distributions for equilibrium. This feature makes the problem of the statistics of stationary nonequilibria particularly interesting and challenging.

In the classical case a rather general model for a system in contact with thermostats is represented in Fig.1, [1].
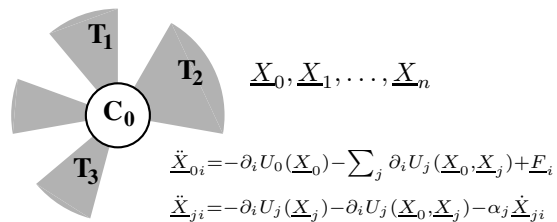

$$\underline{\ddot X}_{0i}=-\partial_i U_0(\underline{X}_0)-\sum_j \partial_i U_j(\underline{X}_0,\underline{X}_j)+\underline{F}_i$$

$$\underline{\ddot X}_{ji}=-\partial_i U_j(\underline{X}_j)-\partial_i U_j(\underline{X}_0,\underline{X}_j)-\alpha_j\underline{\dot X}_{ji}$$

Fig.1 Reservoirs occupy finite regions outside $\mathcal{C}_0$, *e.g.* sectors $\mathcal{C}_j \subset R^3$, $j = 1, 2\ldots$. Their particles (with mass 1) are constrained to have a *total* kinetic energy K_j constant, by suitable forces, so that the reservoirs "temperatures" T_i are well defined. Fixed j the label i is in $1,\ldots.N_j$.

The equations of motion for the particles positions $\underline{X}_0,\underline{X}_1,\ldots,\underline{X}_n$ are written in Fig.1 in terms of

(1) The potential energies for the N_j particles inside each region $\mathcal{C}_j$, $U_j(\underline{X}_j)$, which will be assumed bounded, for simplicity; all masses are $m = 1$, also for simplicity,
(2) The potential energies between particles in $\mathcal{C}_0$ and in $\mathcal{C}_j$: $U_j(\underline{X}_0,\underline{X}_j)$, also assumed bounded,
(3) The external, non conservative, positional forces $\underline{F}$ acting on the particles in $\mathcal{C}_0$,
(4) The thermostat forces $\alpha_i\underline{\dot X}_i$ which are so defined that the total kinetic energy $K_j = \frac{1}{2}\underline{\dot X}_j^2$ in each thermostat is strictly constant. Such forces will be imagined realized by imposing constancy of K_j via *Gauss' principle*, [2, Sec.9]. This gives, [1],

$$\alpha_j \equiv \frac{W_j - \dot U_j}{2K_j} \tag{1.1}$$

where W_j is the work done per unit time by the system particles on the j–th thermostat particles and U_j is the internal potential energy of the j–th reservoir: $W_j = -\underline{\dot X}_j \cdot \boldsymbol{\partial}_{\underline{X}_j} U_j(\underline{X}_0,\underline{X}_j)$. *Thus W_j will be identified with the heat Q_j ceded per unit time by the system to the j-th thermostat.*
(5) The value of the constant K_j will be written $K_j = \frac{3}{2}N_j k_B T_j$ (k_B = Boltzmann's constant) and will define the *temperature* of the j-th thermostat, [1].

A brief computation yields the divergence of the equations of motion, *i.e.* of the phase space contraction rate, for the velocity–position coordinates $\underline{\dot X}, \underline{X}$

$$\sigma(\underline{\dot X}, \underline{X}) = \varepsilon(\underline{\dot X}, \underline{X}) + \dot R(\underline{X}) \tag{1.2}$$

where, remarkably, $\varepsilon(\underline{\dot X}, \underline{X})$ can be interpreted as the *entropy creation rate*

$$\varepsilon(\underline{\dot X}, \underline{X}) = \sum_{j>0} \frac{Q_j}{k_B T_j}, \quad R(\underline{X}) = \sum_{j>0} \frac{U_j}{k_B T_j}, \tag{1.3}$$

Eq.(1.3) are correct up to $O(N^{-1})$ if $N = \min N_j$ as the addends should contain also a factor $(1-\frac{1}{3N_j})$ to be exact:

for simplicity $O(1/N)$ corrections will be ignored (their inclusion would imply trivial changes without affecting the physical interpretation), [1].

An additive total derivative, $\dot{R}(\underline{X})$ in this case, of a bounded quantity does not affect the long time fluctuations. Therefore the average phase space contraction and the average entropy creation rate have the *same average* $\sigma_+ \equiv \varepsilon_+$ and, assuming $\varepsilon_+ \neq 0$, the *same large deviations rate function* $\zeta(p)$ for $p = \frac{1}{\sigma_+ \tau} \int_0^\tau \sigma(S_t(\underline{\dot{X}}, \underline{X}))dt$ and for $\frac{1}{\varepsilon_+ \tau} \int_0^\tau \varepsilon(S_t(\underline{\dot{X}}, \underline{X}))dt$.

Furthermore the equations of motion are *reversible* so that, under the *Chaotic Hypothesis*, the *Fluctuation Theorem* yields, [1, 3–6], the symmetry property

$$\zeta(-p) = \zeta(p) - p\,\varepsilon_+, \qquad |p| < p^* \qquad (1.4)$$

for the large deviations rate $\zeta(p)$ of p. The identification between phase space contraction and entropy creation rate is thus motivated. It should be noted that Eq.(1.3) shows that even in experiments, a case in which one hardly knows the equations of motion and the phase space divergence, the divergence can be measured through heat flow measurements, at least as far as its fluctuations over large time are concerned, and give nontrivial consequences like the fluctuation relation, Eq.(1.4).

2. Quantum systems and thermostats

Is it possible to formulate a dissipation theory analogous to the one developed for classical systems when the quantum nature of the system in $\mathcal{C}_0$ cannot be neglected?

At first it might seem almost impossible: in quantum systems average kinetic energy is *not* identified with temperature; and all motions are quasi periodic if the system is of finite size (as in our examples in Sec.1), so that strictly speaking no chaos is possible.

A way out, explored in the literature, would be to imagine the thermostats as infinite systems whose state far from $\mathcal{C}_0$ is a Gibbs state at a well defined temperature, [7–10]. This is a point of view that could also be taken in the classical case: however the recent progress in classical statistical mechanics was sparked by the introduction of *finite size* thermostat models and this is the path that will be attempted here.

Thermostats have, usually, a macroscopic phenomenological nature: in a way they should be regarded as classical macroscopic objects. Therefore it seems natural to model them as such: thus their temperature can be defined as the average kinetic energy and the question of how to define it does not arise.

Consider the system in Fig.1 when the quantum nature of the particles in $\mathcal{C}_0$ cannot be neglected. Suppose first that the nonconservative force $\underline{F}(\underline{X}_0)$ acting on the system vanishes, *i.e.* consider the problem of heat flow through $\mathcal{C}_0$. Let H be the operator on $L_2(\mathcal{C}_0^{3N_0})$, space of symmetric or antisymmetric wave functions Ψ,

$$-\frac{\hbar^2}{2}\Delta_{\underline{X}_0} + U_0(\underline{X}_0) + \sum_{j>0}\big(U_{0j}(\underline{X}_0, \underline{X}_j) + U_j(\underline{X}_j)\big) \quad (2.1)$$

where $\Delta_{\underline{X}_0}$ is the Laplacian, and note that its spectrum consists of eigenvalues $E_n = E_n(\{\underline{X}_j\}_{j>0})$, for $\underline{X}_j$ fixed.

A system–reservoirs model can be the *dynamical system* on the space of the variables $\big(\Psi, (\{\underline{X}_j\}, \{\underline{\dot{X}}_j\})_{j>0}\big)$ defined by the equations (where $\langle\cdot\rangle_\Psi$ is the expectation in the state Ψ)

$$-i\hbar\dot{\Psi}(\underline{X}_0) = (H\Psi)(\underline{X}_0), \quad \text{and for } j > 0$$

$$\underline{\ddot{X}}_j = -\Big(\partial_j U_j(\underline{X}_j) + \langle\partial_j U_j(\underline{X}_0, \underline{X}_j)\rangle_\Psi\Big) - \alpha_j \underline{\dot{X}}_j \quad (2.2)$$

$$\alpha_j \stackrel{def}{=} \frac{\langle W_j\rangle_\Psi - \dot{U}_j}{2K_j}, \qquad W_j \stackrel{def}{=} -\underline{\dot{X}}_j \cdot \underline{\partial}_j U_{0j}(\underline{X}_0, \underline{X}_j)$$

here the first equation is Schrödinger's equation, the second is an equation of motion for the thermostats particles, [1], similar to the one in Fig.1, whose notation for the particles labels is adopted here too. Evolution maintains the thermostats kinetic energies $K_j \equiv \frac{1}{2}\underline{\dot{X}}_j^2$ exactly constant so that they can be used to define the thermostats temperatures T_j via $K_j = \frac{3}{2}k_B T_j N_j$, as in the classical case.

Let $\mu_0(\{d\Psi\})$ be the *formal* measure on $L_2(\mathcal{C}_0^{3N_0})$

$$\Big(\prod_{\underline{X}_0} d\Psi_r(\underline{X}_0)\, d\Psi_i(\underline{X}_0)\Big)\, \delta\Big(\int_{\mathcal{C}_0} |\Psi(\underline{Y})|^2\, d\underline{Y} - 1\Big) \quad (2.3)$$

with Ψ_r, Ψ_i real and imaginary parts of Ψ. The formal phase space volume element $\mu_0(\{d\Psi\}) \times \nu(d\underline{X}\, d\underline{\dot{X}})$ with

$$\nu(d\underline{X}\, d\underline{\dot{X}}) \stackrel{def}{=} \prod_{j>0}\Big(d\underline{X}_j\, d\underline{\dot{X}}_j\, \delta(\underline{\dot{X}}_j^2 - 3N_j k_B T_j)\Big) \quad (2.4)$$

is conserved, by the unitary property of the wave functions evolution, just as in the classical case, *up to the volume contraction in the thermostats*, [1].

If $Q_j \stackrel{def}{=} \langle W_j\rangle_\Psi$ and R is as in Eq.(1.3) the contraction rate σ of the volume element in Eq.(2.4) is given by Eq.(1.2) with ε, that will be called *entropy creation rate*, defined by Eq.(1.3).

In general solutions of Eq.(2.2) will not be quasi periodic and the Chaotic Hypothesis, [2, 11], can be assumed: if so the dynamics should select an invariant distribution μ. The distribution μ will give the statistical properties of the stationary states reached starting the motion in a thermostat configuration $(\underline{X}_j, \underline{\dot{X}}_j)_{j>0}$ randomly chosen with "uniform distribution" ν on the spheres $\underline{\dot{X}}_j^2 = 3N_j k_B T_j$ and in a random eigenstate of H. The distribution μ, if existing and unique, could be

named the *SRB distribution* corresponding to the chaotic motions of Eq.(2.2).

In the case of a system *interacting with a single thermostat* the latter distribution should be equivalent to the canonical distribution.

Hence an important consistency check for the model proposed in Eq.(2.2) is that there should exist at least one stationary distribution equivalent to the canonical distribution at the appropriate temperature T_1 associated with the (constant) kinetic energy of the thermostat: $K_1 = \frac{3}{2}k_B T_1 N_1$. In the classical case this is an established result, [12],[1, 2].

Hence an important consistency check for the model proposed in Eq.(2.2) is that there should exist at least one stationary distribution μ equivalent to the canonical distribution at the appropriate temperature T_1 associated with the (constant) kinetic energy of the thermostat: $K_1 = \frac{3}{2}k_B T_1 N_1$. In the classical case this is an established result, [12],[1, 2].

The check should be performed also in the present case, thereby providing further motivation and support for the model in Eq.(2.2). A first candidate for μ might be to attribute a probability proportional to $d\Psi\, d\underline{X}_1\, d\underline{\dot{X}}_1$ times

$$\sum_{n=1}^{\infty} e^{-\beta E_n} \delta(\Psi - \Psi_n(\underline{X}_1)\, e^{i\varphi_n})\, d\varphi_n\, \delta(\underline{\dot{X}}_1^2 - 2K_1) \quad (2.5)$$

where Ψ is the wave functions for the system in $\mathcal{C}_0$ and $\dot{X}_1, X_1$ are positions and velocities of the thermostat particles and $\varphi_n \in [0, 2\pi]$ is a phase, $E_n = E_n(\underline{X}_1)$ is the n-th level of $H(\underline{X}_1)$ with $\Psi_n(\underline{X}_1)$ the corresponding eigenfunction. The relation between the distribution in Eq.(2.5) and $\mathrm{EIG}(\rho)$ in [13] should be noted. However, as pointed out by a referee, Eq.(2.5) is not invariant under the evolution Eq.(2.2) and it seems difficult to exhibit explicitly an invariant distribution.

3. Some consequences. Conclusion.

The simplest case arises when $V \equiv 0$: *i.e.* no nonconservative force acts on $\mathcal{C}_0$ and Eq.(2.2) models heat flow, through $\mathcal{C}_0$, between the various reservoirs.

Solutions of Eq.(2.2) are also *reversible*: time reversal being the change in sign of the velocities and the conjugation of the wave function $\Psi(\underline{X}_0)$. Hence under the Chaotic Hypothesis the *Fluctuation Theorem*, [3],[2], see Eq.(1.4), would hold for the entropy creation rate fluctuations in the SRB distribution: however since the phase

space is infinite dimensional corrections to Eq.(1.4) have to be expected for large p, as in [4], and should be discussed on a case by case basis. Note that the fluctuation theorem extension is also here immediate once a model is properly formulated: as it was in the analogous cases of infinite thermostats, [8].

If a nonconservative force $\underline{F}(\underline{X}_0)$ acts on the system and has a (multivalued) potential $V(\underline{X}_0)$, so that $\underline{F}(\underline{X}_0) = -\underline{\partial}V(\underline{X}_0)$ is the force on the particles in $\mathcal{C}_0$, then *in absence of thermostats* generally the system will not reach a stationary state: this is true both in the classical and in the quantum cases. In the latter case the Schrödinger equation, with H modified into $H + V$, will not have eigenvectors because of the multivaluedness of the potential V: actually it will not even be well defined. It should, however, be interpreted as an equation for the wave function Ψ defined on the "covering space" Ω of $\mathcal{C}_0^{3N_0}$ in which the potential $V(\underline{X}_0)$ becomes single valued, and the thermostats should have the effect of allowing reaching a stationary state described by wave functions $\Psi_n(\underline{X}_0 + \underline{\xi}(t))$ with $\Psi_n \in L_2(\Omega)$ and $\underline{\xi}(t)$ a suitable "flow".

Whether this really happens is, however, an open problem even in the classical case; there it has been called the problem of *efficiency* of the thermostats, [1, 14], and it has been studied only in a few numerical simulations involving long range or short range particles interactions. *A fortiori* it is an open problem in the quantum case.

Finally it should be stressed that Eq.(2.2) provides a model of *finite* thermostat for a quantum system and therefore may be suited for simulations and tests.

Identification of phase space contraction rate as the entropy creation rate (up to an additive total time derivative) is an achievement of the recent research in classical nonequilibrium statistical mechanics, [12], which has led to the possibility of nonequilibrium simulations without the need of considering infinite thermostats and, subsequently, to general results like the Fluctuation Theorems, [3],[15, 16], and the possibility to test them experimentally, [17],[1, 18], and even to make use of them in applications. In this note the proposal that rather straightforward extensions to quantum nonequilibrium are possible has been discussed.

[1] G. Gallavotti, Chaos **16**, 043114 (+6) (2006).

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

[3] G. Gallavotti and E. G. D. Cohen, Physical Review Letters **74**, 2694 (1995).

[4] F. Bonetto, G. Gallavotti, A. Giuliani, and F. Zamponi, Journal of Statistical Physics **123**, 39 (2006).

[5] G. Gallavotti, Mathematical Physics Electronic Journal (MPEJ) **1**, 1 (1995).

[6] D. Ruelle, Journal of Statistical Physics **95**, 393 (1999).

[7] J. P. Eckmann, C. A. Pillet, and L. R. Bellet, Communications in Mathematical Physics **201**, 657 (1999).

[8] J. Kurchan, cond-mat/0007360 (2000).

[9] D. Ruelle, Journal of Statistical Physics **98**, 55 (2000).

[10] D. Ruelle, Communications in Mathematical Physics **224**, 3 (2001).

[11] G. Gallavotti and E. G. D. Cohen, Journal of Statistical Physics **80**, 931 (1995).

[12] D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Fluids* (Academic Press, 1990).

[13] S. Goldstein, J. Lebowitz, R. Tumulka, and N.Zanghì, Journal of Statistical Physics **125**, 1193 (2006).

[14] P. Garrido and G. Gallavotti, Journal of Statistical Physics **cond-mat/0607231 and mp_arc 06-197**, doi: 10.1007/s10955 (2007).

[15] G. Gallavotti, Annales de l' Institut H. Poincaré **70**, 429 (1999 and chao-dyn/9703007).

[16] E. G. D. Cohen and G. Gallavotti, Journal of Statistical Physics **96**, 1343 (1999).

[17] F. Bonetto, G. Gallavotti, A. Giuliani, and F. Zamponi, Journal of Statistical Mechanics p. P05009 (2006).

[18] G. Gallavotti, Journal of Statistical Mechanics (JSTAT) pp. P10011 (+9) (2006).