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Thermostats, Chaos and Onsager Reciprocity

Giovanni Gallavotti

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Abstract Finite thermostats are studied in the context of nonequilibrium statistical mechanics. Entropy production rate has been identified with the mechanical quantity expressed by the phase space contraction rate and the currents have been linked to its derivatives with respect to the parameters measuring the forcing intensities. In some instances Green–Kubo formulae, hence Onsager reciprocity, have been related to the fluctuation theorem. However, mainly when dissipation takes place at the boundary (as in gases or liquids in contact with thermostats), phase space contraction may be independent on some of the forcing parameters or, even in absence of forcing, phase space contraction may not vanish: then the relation with the fluctuation theorem does not seem to apply. On the other hand phase space contraction can be altered by changing the metric on phase space: here this ambiguity is discussed and employed to show that the relation between the fluctuation theorem and Green–Kubo formulae can be extended and is, by far, more general.

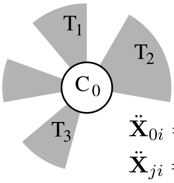
Keywords Nonequilibrium statistical mechanics · Chaotic hypothesis · Fluctuation theorem · Entropy · Large deviations · Thermostats

I am honored to be given this occasion to thank Jürgen Frölich and Tom Spencer for the time they spent discussing with me and communicating their insights, projects and ideas. In particular I have drawn inspiration from the one among the two (JF) with whom I have been in closer contact particularly at the time when he worked at IHES: his strong criticism of any "mathematical deviations" from physical problems has been always extremely effective on my work.

1 Thermostats

A mechanical interpretation of the entropy production rate in nonequilibrium systems interacting with thermostats and possibly subject to external non conservative ("stirring")

G. Gallavotti (✉)
Dipartimento di Fisica and INFN, Università di Roma La Sapienza, P. A. Moro 2, 00185, Rome, Italy
e-mail: giovanni.gallavotti@roma1.infn.it



$$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$$

$$\ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum_j \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i(\mathbf{X}_0)$$
$$\ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i U_j(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

Fig. 1 The $1+n$ boxes $C_0, T_1, \ldots, T_n$ contain $N_0, N_1, \ldots, N_n$ particles, of mass $m = 1$, whose positions and velocities are denoted $\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$, and $\dot{\mathbf{X}}_0, \dot{\mathbf{X}}_1, \ldots, \dot{\mathbf{X}}_n$ respectively. The $\mathbf{E}$ denote external, non conservative, forces and the multipliers α_j model the thermostats and are so defined that the kinetic energies $K_j = \frac{1}{2}\dot{\mathbf{X}}_j^2$ are exactly constants of motion with values $K_j = \frac{3}{2} N_j k_B T_j$, $k_B =$ Boltzmann's constant, $j = 1, \ldots, n$. The energies $U_0, U_j, W_{0,j}$, $j > 0$, should be imagined as generated by pair potentials $\varphi_0, \varphi_j, \varphi_{0,j}$ short ranged, smooth, or with a singularity like a hard core[1]

forces has emerged from simulations and studies on nonequilibrium statistical mechanics since the early 1980's, [1–4]. It is interpreted as phase space contraction rate, as defined by the divergence of the equations of motion which we write symbolically $\dot{x} = f(x)$, *i.e.* $\sigma(x) = -\sum_i \partial_{x_i} f(x)$.

General thermostats acting on a mechanical system, on which also external non conservative forces may act, will be modeled as described in Fig. 1 and illustrated in the caption, [4, 5]:

To imply $\dot{K}_j = 0$ in the above model the multiplier α_j has to be $\alpha_j = -\frac{(Q_j + \dot{U}_j)}{3N_j k_B T_j}$, where

$$Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_{\mathbf{X}_j} W_{0,i}(\mathbf{X}_0, \mathbf{X}_j) \tag{1.1}$$

is naturally interpreted as the *heat* ceded per unit time to the thermostat C_j. The phase space contraction rate, neglecting for simplicity $O(N_j^{-1})$, is computed from the equation in Fig. 1 to be

$$\sigma(X) = \sum_j \frac{Q_j - \dot{U}_j}{k_B T_j} \tag{1.2}$$

(each addend should be multiplied by the factor $(1 - \frac{2}{3N_j})$ if $O(N_j^{-1})$ is not neglected).

Of course $\sigma(x)$ depends upon the metric used on phase space and on the density giving the volume element: both are arbitrary and (1.2) yields the contraction rate for the Euclidean metric and density 1: *i.e.* for the Liouville volume. Because of such ambiguity $\sigma(x)$ *cannot* have an immediate physical meaning. However its time average, and the fluctuations of its finite time averages over long time intervals, have an intrinsic meaning, independent of the choices of the metric and the density, [5], at least if the motions are "chaotic", see below.

Some interesting concrete examples of the above systems are illustrated in Figs. 2 and 3. In Fig. 2 $\alpha = \frac{\mathbf{E}\cdot\dot{\mathbf{x}}}{m\dot{\mathbf{x}}^2}$ and this is an electric conduction model of N charged particles ($N = 2$ in the figure) in a constant electric field $\mathbf{E}$ and interacting with a lattice of obstacles (circles in the figure); it is "autotermostatted" (because C_0 and T_1 coincide) in 2 dimensions. This is a model that appeared since the early days (Drude, 1899, [7]) in a slightly different form

[1] Singularities of different type but care has to be exercised in formulating and by external potentials modeling the containers walls and for simplicity the assumption of smoothness (possibly in presence of a hard core) is made here. For the more general cases, like Lennard-Jones potentials, see [6].

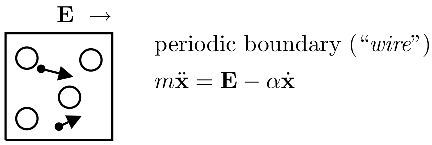


Fig. 2 A modern version of the classical Drude's model for electric conductivity

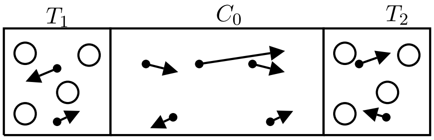


Fig. 3 A model for thermal and electric conduction

(*i.e.* in dimension 3 and with the thermostatting realized by replacing the $-\alpha\dot{\mathbf{x}}$ force with the prescription that after collision with an obstacle velocity is rescaled to $|\dot{\mathbf{x}}| = \sqrt{\frac{3}{m}k_B T}$.

The thermostat forces are a model of the effect of the interactions between the particle (electron) and a background lattice (phonons). This model is remarkable because it is the first nonequilibrium problem that has been treated with real mathematical attention and for which the analog of Ohm's law for electric conduction has been proved if $N = 1$, [8].

Another example is a model of thermal conduction, Fig. 3, in which N_0 hard disks interact by elastic collisions with each other and with other hard disks ($N_1 = N_2$ in number) in the containers labeled by their temperatures T_1, T_2: the latter are subject to elastic collisions between themselves and with the disks in the central container C_0; the separation reflect elastically the particles when their *centers* reach them, thus allowing interactions between the thermostats and the main container particles. Interactions with the thermostats take place only near the separating walls.

If one imagines that the upper and lower walls of the central container are identified (realizing a periodic boundary condition) and that a constant field of intensity E acts in the vertical direction then two forces conspire to keep it out of equilibrium, and the parameters $\mathbf{F} = (T_2 - T_1, E)$ characterize their strength: matter and heat currents flow.

The case $T_1 = T_2$, $E \neq 0$ has been studied in simulations to check that the thermostats are "efficient": *i.e.* that the simple interaction, via collisions taking place across the boundary, is sufficient to allow the systems to reach a stationary state, [9].

Thermostat models similar to the above have been considered in the literature, [3, 10, 11]. A fundamental problem with the model in Fig. 1 is that it is not clear which detailed assumptions have to be made on the interactions to insure that almost all initial conditions evolve staying in a bounded region in phase space so that they can be expected to determine a stationary state. This can be called the "thermostat efficiency problem" and it is, for nonequilibrium, the analogue of the Hamiltonian stability problem in equilibrium, [12]. The experiment in [9] encourages the idea that the assumptions could be very general and fairly simple. In [13] a model like the one in Fig. 3 was studied but the confinement difficulty was avoided by requiring that also the total kinetic energy K_0 in the central container was constant thanks to an extra thermostatting force $-\alpha_0\dot{\mathbf{X}}_0$ with a properly chosen α_0.

The model in Fig. 3 *without* thermostatting forces to keep K_j, $j > 0$ constant, hence with a purely Hamiltonian evolution, has been carefully studied in [14] which also gives the clearest account on the so called "transient fluctuation theorem" improving and extending its earlier formulation in [15], and obtains implicitly also a transient version of the result on fluctuation patterns, analogous to the one derived earlier for steady states in [16].

In [14] there is also a careful analysis of the model in Fig. 3 with the aim of obtaining results for stationary states: stationarity is made possible by taking the thermostats infinitely large stressing the (formidable) problems that one should encounter in attempting a rigorous proof.

In this paper (and in all my preceding ones) I have chosen to consider only finite thermostats with empirical thermostat forces and studied a few problems by introducing a single assumption, the chaotic hypothesis.

2 Chaos

Microscopic motions are in all possible empirical senses "chaotic". The paradigm of chaotic motions are the hyperbolic transitive systems: these are smooth systems whose evolution can be intuitively described by saying that each phase space point moves being seen by the comoving neighboring points as a hyperbolic fixed point.

Another intuitive way to look at such systems is to say that the phase space points can be coded into sequences $\boldsymbol{\xi} = (\xi_i)_{i=-\infty}^{\infty}$ of symbols, say the digits $0, 1, 2, \ldots, q < \infty$, in such a way that the dynamics becomes the trivial shift of the sequence $\boldsymbol{\xi}$, and all sequences which satisfy $M_{\xi_i,\xi_{i+1}} \equiv 1$ represent one phase space point, M being a "compatibility matrix" with elements $M_{ij} = 0, 1$ which is transitive (*i.e.* $M^s_{ij} > 0$ for some s). There may be ambiguities, *i.e.* different sequences may represent the same point, but this can happen on a zero volume set of points only, in close analogy with the familiar ambiguity in the representation of number by digits (where $0.9999\ldots$ and $1.0000\ldots$ are the same number).

It is natural, at least for some [11, 17, 18], to imagine that motions of complex systems, like gases or liquids, are chaotic in the simplest sense (which is also the strongest) of being hyperbolic transitive on the attracting sets (also called Anosov systems). The *chaotic hypothesis*, proposed in [11], see also [12], reflects this remark.

Chaotic hypothesis *Attracting sets for mechanical systems are smooth surfaces on which motion is smooth*, *hyperbolic and transitive*.

This is an hypothesis that has to be considered in the same sense as the ergodic hypothesis for equilibrium statistical mechanics, [19]. Hence *it might be at first disturbing*.

However disturbing assumptions are common in the literature and, nevertheless, are often fruitful. I just mention the assumption of periodicity with equal period ("monocyclicity") of the motions of mechanical systems: it was employed in the derivation of the second law from the action principle in Boltzmann, [20]: this assumption was considered also by Clausius, Maxwell, Helmholtz and was the basis of the early works on the mechanical interpretation of the second law, [21, 22]. At the time there must have been objections to such a bold assumption and someone must have declared, as it was done a little later about its modification into the ergodic hypothesis (and as it is done today about the chaotic hypothesis), that it is "a strong assumption as the periodicity (or ergodicity) hypothesis raises the question of which systems of practical interest are "periodic" ("ergodic"), since almost none of them is actually such", see [23]. Similar statements can be found in the literature, even in good papers.

Chaotic systems (in the above sense) admit a statistics (called SRB statistics, [24–26]), *i.e.* a probability distribution μ on each attracting set which, by integration, gives the average values of the observables $G(x)$ on trajectories whose initial data x are randomly chosen, near enough to an attracting set, with a distribution with some (arbitrary) density:

$$\langle G \rangle = \lim_{T\to\infty} \frac{1}{T} \sum_{j=0}^{T-1} G(S^j x) = \int G(y)\mu(dy), \quad \text{with probability 1} \tag{2.1}$$

where $x \to Sx$ is a discretized time evolution map, obtained by timing observations on the occurrence of some selected event. Or in the (unphysical, yet customary and interesting) case of observations in continuous time

$$\langle G\rangle = \lim_{T\to\infty} \frac{1}{T}\int_0^T G(S_t x)\,dt = \int G(y)\mu(dy), \quad \text{with probability 1} \tag{2.2}$$

where $x \to S_t x$ denotes the evolution of the initial data x via the equations of motion, [27].

If motion is chaotic (*i.e.* hyperbolic, regular, transitive) the finite time averages

$$\gamma = \langle G\rangle_\tau = \frac{1}{\tau}\sum_{j=0}^{\tau-1} G(S^j x) \tag{2.3}$$

satisfy a *large deviations law*, *i.e.* fluctuations off the average $\langle G\rangle$ as large as τ itself are controlled by a function $\zeta(\gamma)$ convex and analytic in a (finite) interval (γ_1,γ_2), maximal at $\langle G\rangle$. This means that the probability that $\gamma\in[a,b]$ satisfies

$$P_\tau(\gamma\in[a,b]) \simeq e^{\tau \max_{[a,b]}\zeta(\gamma)}, \quad \forall a,b\in(\gamma_1,\gamma_2) \tag{2.4}$$

and the interval (γ_1,γ_2) is non trivial if $\langle G^2\rangle - \langle G\rangle^2 > 0$, [24, 28, 29]. If $\zeta(\gamma)$ is quadratic at its maximum (*i.e.* at $\langle G\rangle$) then this implies a central limit theorem for the fluctuations of $\sqrt{\tau}\langle G\rangle_\tau$, but (3.4) is a much stronger property.

Remarks

(1) The hypothesis holds also in equilibrium; if the system admits a dense trajectory in phase space it implies the classical ergodic hypothesis.
(2) If the observable G has nonzero SRB-average it is convenient to consider instead the observable $\frac{G}{\langle G}\rangle$ because it is dimensionless, just as in the case of $\langle G\rangle = 0$ it is convenient to consider the dimensionless observable $\frac{G}{\sqrt{\langle G^2\rangle}}$.
(3) If the dynamics is *reversible*, *i.e.* there is a smooth, isometric, map I of phase space such that $I^2 = 1$ and $IS_t = S_{-t}I$ or in the discrete case $IS = S^{-1}I$, then any *time reversal odd* observable G, with non zero average and nonzero dispersion $\langle G^2\rangle - \langle G\rangle^2 > 0$, is such that the interval of (γ_1,γ_2) of large deviations for $\frac{G}{\langle G\rangle}$ is at least $(-1,1)$ provided there is a dense orbit (which also implies existence of only one attracting set).
(4) The systems in the thermostats model of Sect. 1 are all reversible with I being the ordinary time reversal, change in sign of velocity with positions unaltered, and the phase space contraction $\sigma(x)$ is odd under time reversal, see (1.2). Therefore if $\sigma_+ = \langle\sigma\rangle > 0$ it follows that the observable

$$p' = \frac{1}{\tau}\sum_{j=0}^{\tau-1}\frac{\sigma(S^j x)}{\sigma_+} \tag{2.5}$$

has domain of large deviations of the form $(-\overline{g},\overline{g})$ and contains $(-1,1)$.
(5) Since by (1.2) σ differs from $\varepsilon(x) = \sum_{j>0}\frac{Q_j}{k_B T_j}$ by the time derivative of an observable, it follows that the finite or infinite time averages σ and of ε have, for large τ, the same distribution. Therefore the same large deviations function $\zeta(p)$ controls the fluctuations

of p' above and of

$$p = \frac{1}{\tau}\sum_{j=0}^{\tau-1}\frac{\varepsilon(S^j x)}{\sigma_+}, \quad \sigma_+ \equiv \langle\sigma\rangle_{SRB} = \langle\varepsilon\rangle_{SRB}, \tag{2.6}$$

and it has been shown, [11, 30] and in a mathematical form in [31], that under the chaotic hypothesis and reversibility of motions on the attracting set, the function $\zeta(p)$ has the symmetry property

$$\zeta(-p) = \zeta(p) - p\sigma_+, \quad \text{for all } p \in (-\overline{p}, \overline{p}) \tag{2.7}$$

and $\overline{p} \geq 1$. This is the *fluctuation theorem* of [11] (it requires a proof and therefore it should not be confused with several identities, see for instance [32], with which, for reasons that I fail to understand, it has been often identified). The interest of the theorem is that it is *universal*, model independent yielding a parameter free relation which deals with a quantity which has the physical meaning of entropy production rate and therefore has an independent macroscopic definition and is accessible to experiments.

(6) Equation (2.7) is closely related to the theorem in [14], from which it differs only because it deals with finite thermostats assuming the (strong) chaotic hypothesis, rather than dealing with infinite thermostats and assuming (strong) ergodicity properties. In spite of the latter work several paper have appeared in the literature trying to get rid of the chaotic hypothesis without adding much (if anything) to the lucid discussion in [14] about the necessity of suitable assumptions in order to allow extending a transient fluctuation relation (which is an identity, requiring no assumption, on the full phase space, [32]) to a stationary one (which deals with properties that hold on a subset of zero probability with respect to the initial data sampling).

(7) The fluctuation theorem has several extensions including a remarkable, parameter free relation that concerns the relative probability of patterns of evolution of an observable and their reversed patterns, [12, 33, 34], related to the Onsager–Machlup fluctuations theory, which keeps being rediscovered in various forms and variations in the literature.

3 Onsager Reciprocity

Another consequence of the fluctuation theorem are the Onsager reciprocity and Green–Kubo formulae for the infinitesimal deviations from equilibrium, [13]; the latter can be independently derived (in a simpler way) from the chaotic hypothesis and time reversal symmetry assumed only at equilibrium, [8], as it will be shown in the concluding comments, or as discussed from a somewhat different viewpoint in [35].

Here the aim is to show that *the Green–Kubo formulae, hence Onsager's reciprocity, can be regarded as the version at zero forcing of the fluctuation theorem for stationary states*.

In the case in which $T_1 = T_2 = \cdots = T$ and $\mathbf{E} = \mathbf{0}$ the system is in thermal equilibrium and its state is characterized by a probability distribution μ_0 which invariant under the time evolution $x \to S_t x$ generated by the equations in Fig. 1. Setting $x = (\mathbf{X}_0, \dot{\mathbf{X}}_0, \mathbf{X}_1, \dot{\mathbf{X}}_1, \ldots, \mathbf{X}_n, \dot{\mathbf{X}}_n)$ it is remarkable that the distribution can be explicitly found, [3], as

$$\mu_0(dx) = const\, e^{-\beta(U_0(\mathbf{X}_0)+\sum_{j>0}(U_j(\mathbf{X}_j)+W(\mathbf{X}_0,\mathbf{X}_j))+K_0(\dot{\mathbf{X}}_0))} \times \Big(\prod_{j>0}\delta\Big(K_j - \frac{3}{2}N_j T\Big)\Big)\Big(\prod_{j\geq 0} d\dot{\mathbf{X}}_j\, d\mathbf{X}_j\Big) \tag{3.1}$$

where $\beta = \frac{1}{k_B T}$ (neglecting $O(N_j^{-1})$ for simplicity). Calling the "unperturbed" energy $H_0(x) = K_0(\dot{\mathbf{X}}_0) + \sum_{j\ge 0} U_j(\mathbf{X}_j) + \sum_{j>0} W_j(\mathbf{X}_0, \mathbf{X}_j)$[2] and $\widetilde{\delta}(\mathbf{K}_j(x), T_j) = \delta(K_j(\dot{\mathbf{X}}_j) - \frac{3}{2} N_j T_j))$, (3.1), written more compactly, is

$$\mu_0(dx) = const\, e^{-\beta H_0(x)} \prod_{j>0} \widetilde{\delta}(K_j(x), T)\, dx \tag{3.2}$$

which is a distribution in an ensemble which, for the system in C_0, is equivalent to the canonical one (for $N_0, L_0 \to \infty$, $N_0/L_0^3 = const$ if L_0 is the side of the container).

We now want to compare the average values of various currents that are switched on when $\mathbf{E}$, the external forces, become non zero and the temperatures of the thermostats become different: $\mathbf{E} \neq \mathbf{0}$ and $T_j = T + \varepsilon_j$. More precisely we look for the relations between infinitesimal forcing *actions* and the corresponding *currents*, *i.e.* the susceptibility coefficients.

The currents are related to the average values of the derivatives of the entropy production with respect to the forces (material currents) or to the temperature inequalities (heat currents). *However* the arbitrariness inherent in the phase space contraction generates interesting questions: for instance in the model in Fig. 1 the phase space contraction with respect to the Liouville volume *is independent of the external forces* $\mathbf{E}$, see (1.1), (1.2), so that $\partial_E \sigma \equiv 0$, while it is *obvious* that the external forces generate material currents, being non conservative.

On the other hand even in equilibrium a thermostatted system exchanges heat with the thermostats: hence there is a production of entropy which has a zero average but which is not zero and equal to $\sum_j \frac{Q_j}{k_B T}$.

It is therefore interesting to see, first, why in equilibrium (*i.e.* when the thermostats have all the same temperature and no external forces act) the SRB-average of $\sum_j \frac{Q_j}{k_B T}$ vanishes, [36]. This is the case because the latter quantity is the derivative of $\beta H_0(x)$. In fact the derivative βH_0 is β times the work done on the system by the forces $-\alpha \dot{\mathbf{X}}_j$ which equals $\sum_{j>0} \frac{Q_j - \dot{U}_j}{k_B T}$. This means that $\sigma(x) - \beta \dot{H}_0(x) \equiv 0$ and therefore

$$\sum_{j>0} \frac{Q_j}{k_B T} = \beta \dot{H}_0(x) + \sum_{j>0} \frac{\dot{U}_j(x)}{k_B T} \tag{3.3}$$

and the r.h.s. is a time derivative, hence it has 0 time average.

When the system is out of equilibrium (*i.e.* $T_j \not\equiv T$ and $\mathbf{E} \neq \mathbf{0}$) the heat currents flowing into the thermostats divided by the temperature are generated by the entropy production rate $j_k(x) = \partial_{T_k} \sigma(x)$, while the material currents through the system are defined by minus the derivatives with respect to the acting forces of the work per unit time that they do, given by the corresponding derivatives of $\dot{H}_0$. Thus given arbitrarily β the quantity

$$\overline{\sigma}(x) = \sigma(x) - \beta \dot{H}_0(x) \tag{3.4}$$

[2] The kinetic energy of the thermostats is an additive constant and therefore is not explicitly written.

generates all currents up to a proportionality factor (here β is arbitrary). It can be computed as

$$\overline{\sigma}(x) = \sum_{j>0} \frac{Q_j - \dot U_j}{k_B T_j} - \beta \mathbf{E} \cdot \dot{\mathbf{X}}_0 - \beta \sum_{j>0} (Q_j - \dot U_j) \tag{3.5}$$

because, by the equations in Fig. 1, $\dot H_0 = \mathbf{E} \cdot \dot{\mathbf{X}}_0 - \sum_{j>0} \alpha_j \dot{\mathbf{X}}_j^2$ and therefore $\dot H_0 = \mathbf{E} \cdot \dot{\mathbf{X}}_0 + \sum_{j>0} (Q_j - \dot U_j)$, see (1.1).

Hence, discarding the time derivatives terms involving the $\dot U_j$ (parameters independent), the currents (at infinitesimal forcing) can be generated by the function

$$\sigma_0(x) = \sum_{j>0} Q_j \left(\frac{1}{k_B T_j} - \frac{1}{k_B T} \right) - \mathbf{E} \cdot \dot{\mathbf{X}}_0 \frac{1}{k_B T} \tag{3.6}$$

The generating function σ_0 is odd under time reversal and *vanishes at equilibrium* $T_j = T_i$, $\mathbf{E} = \mathbf{0}$ if T is chosen $T = T_j$; its derivatives with respect to the forcing parameters T_j, E_k generate the heat and material currents and, at the same, time $\sigma_0(x)$ differs from the phase space contraction by a time derivative.

Note that $\overline{\sigma}$ is also the phase space contraction of the volume in phase space, *provided* the latter is measured by the distribution

$$\overline{\mu}(dx) = const\, e^{-\beta H_0(x)} \prod_{j>0} \widetilde{\delta}(K_j(x), T_j)\, dx \tag{3.7}$$

In [37] a reversible system (like the model in Fig. 1), has been considered in which the generating function for the currents σ_0 *vanishes for vanishing "thermodynamic forces"* $\mathbf{F} = (T_1 - T, \ldots, T_n - T, E_1, \ldots, E_q) = \mathbf{0}$ and satisfies the fluctuation relation or, better, its extension in [37, (14)], has been considered.

And it has been shown, [37], that the products of the currents, generated by the thermodynamic forces, times $\beta = \frac{1}{k_B T}$, and defined by

$$j_m = \partial_{F_r} \overline{\sigma}(x) \equiv \partial_{F_r} \sigma_0(x) \tag{3.8}$$

are such that their averages $J_m = \langle j_m \rangle_{SRB}$ have susceptibilities $L_{mp} = \partial_{F_m} J_p|_{\mathbf{F}=\mathbf{0}}$ which satisfy

$$L_{mp} = \frac{1}{2} \int_{-\infty}^{\infty} dt \big(\langle j_m(S_t \cdot) j_p(\cdot) \rangle_{SRB} - \langle j_m \rangle_{SRB} \langle j_p \rangle_{SRB} \big) \big|_{\mathbf{F}=\mathbf{0}} \tag{3.9}$$

If the parameter β is properly chosen as mentioned above, *i.e.* $\beta = \frac{1}{k_B T}$ (and only if so chosen), σ_0 will vanish when $\mathbf{F} = \mathbf{0}$. Since $\overline{\sigma}$ and σ_0 differ by a time derivative they can be interchangeably used in the theory of the SRB distribution and therefore σ_0 satisfies the fluctuation theorem (because $\overline{\sigma}$ does); the assumptions in the derivation in [37] apply and therefore (3.9) yields Onsager's reciprocity $L_{mp} = L_{pm}$, and Green–Kubo formula.

4 Work and Entropy Theorems. Comments

(1) This extends considerably the results in [13, 37] removing the restriction on the phase space contraction to be the generating function of the currents. The key is that the phase

space contraction is only defined up to a time derivative of an observable and the generating function of the currents coincides with the phase space contraction only if the observable is properly chosen.

(2) it is worth stressing that the extension of the fluctuation theorem needed to derive from it Onsager reciprocity is an important one: in [33] it was further extended to show (*conditional reversibility theorem*) that there is a simple relation between the probability that an observable $F(x)$, even or odd under time reversal (for simplicity), follows in a time interval $-\tau, \tau$ a "pattern" $F(S_t x) = \varphi(t)$ or the "reversed pattern" $F(S_t x) = \varphi(-t)$ *provided* the entropy production rate is fixed, [33]. A statement that can be colorfully quoted as … *relative probabilities of patterns observed in a time interval of size τ and in presence of an average entropy production p are the same as those of the corresponding anti-patterns in presence of the opposite average entropy production rate*, [34, p. 476], or also [34, p. 476], or … *it "suffices" to change the sign of the entropy production to reverse the arrow of time*, or also … *a waterfall will go up, as likely as we see it going down, in a world in which for some reason, or by the deed of a Daemon, the entropy creation rate has changed sign during a long enough time*, [12, p. 288]. We can also say that the motion on an attractor is reversible, even in the presence of dissipation, once the dissipation is fixed. Again variations of this property keep being rediscovered, see for instance [38].

(3) In the case of systems in contact with a single thermostat but in a stationary nonequilibrium because of the action of external forces the above analysis has also interesting consequences. The phase space contraction can be written as $\sigma(x) = \sum_{j>0} \frac{Q_j - \dot{U}_j}{k_B T}$, as in (1.2), or by adding to it a time derivative as $\overline{\sigma}(x) = \sigma(x) + \beta \dot{H}_0(x)$ which in this case is simply $\overline{\sigma}(x) = \frac{\mathbf{E}(\mathbf{X}_0)\cdot\dot{\mathbf{X}}_0}{k_B T} = \frac{\dot{W}}{k_B T}$. Therefore the fluctuation theorem, as pointed out by Bonetto: see [12, (9.10.4)], yields the following "*work theorem*"

$$\langle e^{-\beta w \tau}\rangle_{SRB} = 1, \qquad w \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau \dot{W}(S_t x)\, dt \tag{4.1}$$

in the sense that the logarithm of the l.h.s. divided by τ tends to 0 as $\tau \to \infty$. More generally the identity up to a time derivative of σ, $\overline{\sigma}$, $\sum_{j>0} \frac{Q_j}{k_B T_j}$ and $\sigma_0 = \sum_{j>0} (\frac{Q_j}{k_B T_j} - \beta Q_j) - \beta \mathbf{E} \cdot \dot{\mathbf{X}}_0$, see (3.3)–(3.6), implies that, in the same sense as in (4.1), the finite time average P of *any* of the latter four quantities, denoted $\widetilde{\sigma}$, over a time τ will satisfy

$$\langle e^{-P\tau}\rangle_{SRB} = 1, \qquad P \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau \widetilde{\sigma}(S_t x) \tag{4.2}$$

which can be called an "*entropy theorem*": not only remarkable because it involves quantities that can be measured in experiments, [4], but also because here β can be taken *arbitrary*, so that (4.2) is an infinite number of relations. Actually if $p = P/\langle\sigma_0\rangle_{SRB}$ the large deviations of p satisfy the fluctuation theorem symmetry (2.7). Note however that all such relations are special cases of the theorem in [16].

(4) A further alternative method to derive the Green–Kubo relations is in [39]. It will be illustrated, for completeness, in the simple case of a system interacting with only one thermostat and subject to several nonconservative external forces that will be proportional to parameters $\mathbf{E} = (E_1, \dots, E_q)$. Under the chaotic hypothesis the SRB average of the currents $J_m = \int \mu_{SRB}(dx) j_m(x)$, with $j_m(x) \stackrel{def}{=} \partial_{E_m} \overline{\sigma}(x)$ in presence of thermodynamic forces $\mathbf{E}$, can be computed as the limit $J_m = \lim_{t\to\infty} \mu_0(j_m(S_t^{\mathbf{E}} x))$, if $S_t^{\mathbf{E}}$ is the

map such that $x \to S_t^{\mathbf{E}} x$ solves the equations of motion in presence of forcing forces with parameters $\mathbf{E}$, and μ_0 is the equilibrium distribution (3.1), [8, 39]. Therefore

$$\begin{aligned} J_m &= \lim_{t\to\infty} \mu_0(j_m(S_t^{\mathbf{E}}x)) = \int_0^{+\infty} dt \frac{d}{dt} \int \mu_0(dx) J_m(S_t^{\mathbf{E}}x) \\ &= \int_0^{+\infty} dt \frac{d}{dt} \int \frac{\mu_0(dx)}{\mu_0(dS_t^{\mathbf{E}}x)} \mu_0(dS_t^{\mathbf{E}}x) j_m(S_t^{\mathbf{E}}x) \\ &= \int_0^{+\infty} dt \frac{d}{dt} \int \frac{\mu_0(dS_{-t}^{\mathbf{E}}x)}{\mu_0(dx)} \mu_0(dx) j_m(x) \end{aligned} \tag{4.3}$$

but by the comment preceding (3.7) (considered with $T_j \equiv T$)

$$\frac{d}{dt} \frac{\mu_0(dS_{-t}^{\mathbf{E}}x)}{\mu_0(dx)} = \overline{\sigma}(S_{-t}^{\mathbf{E}}x) \tag{4.4}$$

so that the chain of equalities in (4.3) yields

$$J_m = \int_0^{\infty} dt \int \overline{\sigma}(S_{-t}^{\mathbf{E}}x) j_m(x) \mu_0(dx) \tag{4.5}$$

And taking into account that $\overline{\sigma}(x) \equiv 0$, if $\mathbf{E} = \mathbf{0}$, and $j_m(x) = \partial_{E_m} \overline{\sigma}(x)$

$$\begin{aligned} L_{pm} &= \partial_{E_p} J_m|_{\mathbf{E}=\mathbf{0}} = \int_0^{\infty} dt \bigg(\int \partial_{E_p} \overline{\sigma}(S_{-t}^{\mathbf{E}}x) \partial_{E_m} \overline{\sigma}(x) \mu_0(dx) \bigg) \bigg|_{\mathbf{E}=\mathbf{0}} \\ &= \frac{1}{2} \int_{-\infty}^{\infty} dt \bigg(\int \partial_{E_p} \overline{\sigma}(S_{-t}^{\mathbf{E}}x) \partial_{E_m} \overline{\sigma}(x) \mu_0(dx) \bigg) \bigg|_{\mathbf{E}} = \mathbf{0} = L_{mp} \end{aligned} \tag{4.6}$$

by time reversal invariance of the equilibrium distribution μ_0, which is the Green–Kubo formula.

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