

# Chaotic dynamics, fluctuations, nonequilibrium ensembles

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The ideas and the conceptual steps leading from the ergodic hypothesis for equilibrium statistical mechanics to the chaotic hypothesis for equilibrium and nonequilibrium statistical mechanics are illustrated. The fluctuation theorem linear law and universal slope prediction for reversible systems is briefly derived. Applications to fluids are briefly alluded to. © 1998 American Institute of Physics. [S1054-1500(98)01702-9]

A deterministic, many particle system subject to external nonconservative forces evolves towards a stationary state when also subject to the action of "thermostatting" forces that keep the total mechanical energy from indefinitely increasing. Such forces must be dissipative and the stationary state will be described by a probability distribution that is concentrated on a zero volume attractor. Therefore, in such systems, the fundamental problem of which is the appropriate nonequilibrium extension of the Boltzmann-Maxwell-Gibbs distribution becomes particularly evident. Ruelle proposed (1973) a solution to a similar problem that arises in the theory of turbulence ("which is the distribution on the velocity fields that describes the stationary state of a turbulent Navier-Stokes flow?"). His proposal applies equally well to nonequilibrium statistical mechanics, as suggested in recent papers, and is described here under the name "chaotic hypothesis." It is argued that the latter is a generalization of the ergodic hypothesis and that it leads to a concrete representation of stationary distributions. We suggest that the interest of the hypothesis lies in its fundamental nature (i.e., it should hold "essentially without restrictions") and in being, at the same time, compatible with the ergodic hypothesis and hence in being a genuine extension of the latter to systems out of equilibrium. We review how, in certain special systems, it can be used to derive concrete results (the "fluctuation theorem") which have been tested against several numerical experiments. It is also compatible with the classical linear response theory of Onsager and Green Kubo which, quite generally, is implied by the hypothesis.

## I. ERGODIC HYPOTHESIS

Giving up a detailed description of microscopic motion led to a statistical theory of macroscopic systems and to a deep understanding of their equilibrium properties. At the same time a far less successful (even for steady states theory) approach to nonequilibrium systems began.

It is clear today, as it already was to Boltzmann and many others, that some of the assumptions and guiding ideas used in building up the theory were not really necessary or, at least, could be greatly weakened or just avoided.

A typical example is the *ergodic hypothesis*. It is interesting to include a very short history of it (as I see it). Early

on, Boltzmann started publishing the first version of the *heat theorem*. The theorem states that one can define in terms of time averages of total or kinetic energy, of density, and of average momentum transfer to the container walls, quantities that one could call *specific internal energy*  $u$ , *temperature*  $T$ , *specific volume*  $v$ , *pressure*  $p$  and when two of them vary, say the specific energy and volume by  $du$  and  $dv$ , they verify:

$$\frac{du + p dv}{T} = \text{exact.} \quad (1)$$

At the beginning, this was discussed in very special cases (like free gases). However, about 15 years later Helmholtz noted in a series of four ponderous papers that for a class of very special systems, that he called *monocyclic*, in which all motions were periodic and in a sense nondegenerate, one could give appropriate names, familiar in macroscopic thermodynamics, to various mechanical averages and then check that they verified the relations that would be expected between thermodynamic quantities with the same name.

Helmholtz' assumptions about monocyclicity are very strong and I do not see them satisfied other than in confined one dimensional Hamiltonian systems. Here is an example of Helmholtz' reasoning (as reported by Boltzmann).

Consider a one-dimensional system with potential  $\varphi(x)$  such that  $|\varphi'(x)| > 0$  for  $|x| > 0$ ,  $\varphi''(0) > 0$  and

$$\varphi(x) \xrightarrow{x \rightarrow \infty} +\infty$$

(in other words a one-dimensional system in a confining potential). There is only one motion per energy value (up to a shift of the initial datum along its trajectory) and all motions are periodic so that the system is *monocyclic*. We suppose that the potential  $\varphi(x)$  depends on a parameter  $V$ .

One defines *state* as a motion with given energy  $E$  and given  $V$ , and  $U$ =total energy of the system  $\equiv K + \varphi$ ,  $T$ =time average of the kinetic energy  $K$ ,  $V$ =the parameter on which  $\varphi$  is supposed to depend, and  $p$ =time average of  $\partial_V \varphi$ .

A state is parametrized by  $U, V$  and if such parameters change by  $dU, dV$ , respectively, we define:

$$dL = -p dV, \quad dQ = dU + p dV \quad (2)$$

then:

*Theorem (Helmholtz): the differential  $(dU + p dV)/T$  is exact.*

In fact let

$$S = 2 \log \int_{x_-(U,V)}^{x_+(U,V)} \sqrt{K(x;U,V)} dx$$

$$= 2 \log \int_{x_-(U,V)}^{x_+(U,V)} \sqrt{U - \varphi(x)} dx \quad (3)$$

( $\frac{1}{2}S$  is the logarithm of the action), so that

$$dS = \frac{\int (dU - \partial_V \varphi(x) dV) \frac{dx}{\sqrt{K}}}{\int K \frac{dx}{\sqrt{K}}} \quad (4)$$

and, noting that  $dx/\sqrt{K} = \sqrt{2/m} dt$ , we see that the time averages are given by integrating with respect to  $dx/\sqrt{K}$  and dividing by the integral of  $1/\sqrt{K}$ . We find therefore

$$dS = \frac{dU + p dV}{T}. \quad (5)$$

Boltzmann saw that this was not a simple coincidence: his interesting (and healthy) view of the continuum (which he probably never really considered as more than a convenient artifact, useful for computing quantities describing a discrete world) led him to think that in some sense *monocyclicity was not a strong assumption*.

Motions tend to recur (and they do in systems with discrete phase space) and in this light monocyclicity would simply mean that, waiting long enough, the system would come back to its initial state. Thus, its motion would be monocyclic and one could try to apply Helmholtz' ideas (in turn based on his own previous work) and perhaps deduce the heat theorem in great generality. The nondegeneracy of monocyclic systems becomes the condition that for each energy there is just one cycle and *the motion visits successively all (discrete) phase space points*.

Taking this viewpoint one had the possibility of checking that in all mechanical systems one could define quantities that one could name with "thermodynamic names" and that would verify properties coinciding with those that thermodynamics would predict for quantities with the same name.

He then considered the two body problem, showing that the thermodynamic analogies of Helmholtz could be extended to systems which were degenerate, but still with all motions periodic. This led to somewhat obscure considerations that seemed to play an important role for him, given the importance he gave them. They certainly do not help in encouraging the reading of his work: the breakthrough paper of 1884<sup>1</sup> starts with associating quantities with a thermodynamic name to Saturn's rings (regarded as rigid rotating rings!) and checking that they verify the right relations [like the second law, see Eq. (1)].

In general, one can call *monocyclic* a system with the property that there is a curve  $\ell \rightarrow x(\ell)$ , parametrized by its curvilinear abscissa  $\ell$ , varying in an interval  $0 < \ell < L(E)$ , closed and such that  $x(\ell)$  covers all the positions compatible with the given energy  $E$ .

Let  $x = x(\ell)$  be the parametric equations so that the energy conservation can be written

$$\frac{1}{2} m \dot{\ell}^2 + \varphi(x(\ell)) = E, \quad (6)$$

then if we suppose that the potential energy  $\varphi$  depends on parameter  $V$  and if  $T$  is the average kinetic energy,  $p = -\langle \partial_V \varphi \rangle$  it is, for some  $S$ ,

$$dS = \frac{dE + p dV}{T}, \quad p = -\langle \partial_V \varphi \rangle, \quad T = \langle K \rangle \quad (7)$$

where  $\langle \cdot \rangle$  denotes time average.

A typical case to which the above can be applied is that in which the whole space of configurations is covered by the projection of a single periodic motion and the whole energy surface consists of just one periodic orbit, or at least only the phase space points that are on such orbit are observable. Such systems provide, therefore, natural models of thermodynamic behavior.

Noting that a chaotic system like gas in a container of volume  $V$ , which can be regarded as a parameter on which the potential  $\varphi$  (which *includes* interaction with the container walls) depends, will verify "for practical purposes" the above property, we see that we should be able to find a quantity  $p$  such that  $dE + p dV$  admits the average kinetic energy as an integrating factor.

On the other hand the distribution generated on the surface of constant energy by the time averages over the trajectory should be an invariant distribution and therefore a natural candidate for it is the uniform distribution, *Liouville's distribution*, on the surface of constant energy. The only one if we accept the viewpoint, probably Boltzmann's, that phase space is discrete and motion on the energy surface is a monocyclic permutation of its finitely many cells (ergodic hypothesis). It follows that if  $\mu$  is the Liouville distribution and  $T$  is the average kinetic energy with respect to  $\mu$  then there should exist a function  $p$  such that  $T^{-1}$  is the integrating factor of  $dE + p dV$ .

Boltzmann shows that this is the case and, in fact,  $p$  is the average momentum transfer to the walls per unit time and unit surface, i.e., it is the *physical* pressure.

Clearly this is not a proof that the equilibria are described by the microcanonical ensemble. However, it shows that for most systems, independently of the number of degrees of freedom, one can define a *mechanical model of thermodynamics*.

Thermodynamic relations are *very general* and simple consequences of the structure of the equations of motion. They hold for small and large systems, from 1 degree of freedom to  $10^{23}$  degrees. The above arguments, based on a discrete view of phase space, suggest that they hold in some approximate sense (as we have no idea on the precise nature of the discrete phase space). But they may hold *exactly* even for small systems, if suitably formulated: for instance in the 1884 paper<sup>1</sup> Boltzmann shows that in the *canonical ensemble* the relation Eq. (1) (i.e., the second law) holds *without corrections* even if the system is small.

Thus the ergodic hypothesis does help in finding out why there are mechanical "models" of thermodynamics:

they are ubiquitous in small and large systems. But such relations are of interest in large systems and not really in small ones.

For large systems any theory claiming to rest on the ergodic hypothesis may seem bound to fail because if it is true that a system is ergodic, it is also true that the time the system takes to go through one of its cycles is simply too long to be of any interest and relevance: this was pointed out very clearly by Boltzmann<sup>2</sup> and earlier by Thomson.

The reason we observe the approach to equilibrium over time scales far shorter than the recurrence times is due to the property that the microcanonical ensemble is such that *on most of phase space the actual values of the observables, whose averages yield the pressure and temperature and the few remaining thermodynamic quantities, assume the same value.*<sup>3</sup> This implies that such value coincides with the average and therefore verifies the *heat theorem*, if  $p$  is the pressure (defined as the average momentum transfer to the walls per unit time and unit surface).

The ergodic hypothesis loses its importance and fundamental nature and appears simply as a tool used in understanding that some of the relations that we call “macroscopic laws” hold in some form for *all* systems, whether small or large.

## II. THE CHAOTIC HYPOTHESIS

A natural question is whether something similar to the above development can be achieved in systems out of equilibrium. I am not thinking of systems evolving in time: rather I refer to properties of systems that reach a stationary state under the influence of external nonconservative forces acting on them. For instance, I think of an electric circuit in which a current flows (stationarily) under the influence of an electro-motive field; or of a metal bar with two different temperatures fixed at the extremes; or of a Navier–Stokes fluid in a Couette flow.

The first two systems, regarded as microscopic systems (i.e., as mechanical systems of particles), do certainly have very chaotic microscopic motions even in the absence of external driving (while macroscopically they are in a stationary state and nothing happens, besides a continuous, sometimes desired, heat transfer from the system to the surroundings). The third system also behaves, as a macroscopic system, very chaotically at least when the Reynolds number is large.

Can one do something similar to what Boltzmann did?

The first problem is that the situation is quite different: there is no established nonequilibrium thermodynamics to guide us. The great progress of the theory of stationary nonequilibrium that took place in the past century (I mean the twentieth), at least the ones that are unanimously recognized as such, only concern properties of *incipient* nonequilibrium: i.e., transport properties at vanishing external fields (I think here of Onsager’s reciprocity and its quantitative form given by Green–Kubo’s transport theory). So it is by no means clear that there is any general nonequilibrium thermodynamics.

Nevertheless, in 1973 a first suggestion that a general

theory might be possible for nonequilibrium systems in stationary and chaotic states was made by Ruelle in talks and eventually in papers.<sup>4</sup>

The proposal is very ambitious as it suggests a *general and essentially unrestricted* answer to which should be the ensemble that describes stationary states of a system, *whether in equilibrium or not*.

The ergodic hypothesis led Boltzmann to the general theory of ensembles (as acknowledged by Gibbs, whose work has been perhaps the main channel through which the allegedly obscure works of Boltzmann reached us): besides giving the second law, Eq. (1), it also prescribed the microcanonical ensemble for describing equilibrium statistics.

The reasoning of Ruelle was that from the theory of simple chaotic systems one knew that such systems, for the simple fact that they are chaotic, will reach a “unique” stationary state. Therefore, simply assuming chaoticity would be tantamount to assuming that there is a uniquely defined ensemble which should be used to compute the statistical properties of a system out of equilibrium.

Therefore one is, in a very theoretical way, in a position to inquire whether such a unique ensemble has *universal properties* valid for small and large systems alike: of course we cannot expect too many of them to hold. In fact in equilibrium theory the only one I know precisely is the heat theorem, besides a few general (related) inequalities (e.g., *positivity of the specific heat or of compressibility*). The theorem leads, indirectly as we have seen, to the microcanonical ensemble and then, after one century of work, to a rather satisfactory theory of phenomena like phase transitions, phase coexistence, and universality.

In the end, the role of the ergodic hypothesis emerges, at least in my view, as greatly enhanced: and the idea of Ruelle seems to be its natural (and I feel unique) extension out of equilibrium.

Of course this would suffer from the same objections that are continuously raised about the ergodic hypothesis: namely “there is the time scale problem.”

To such objections, I do not see why the answer given by Boltzmann should not apply *unchanged*: large systems have the extra property that the interesting observables take the same value in the whole (or virtually whole) phase space. *Therefore they verify any relation that is true no matter whether the system is large or small*: such relations (whose very existence is, in fact, surprising) might be of no interest whatsoever in small systems (like in the above mentioned Boltzmann’s rigid Saturn ring, or in his other similar example of the Moon regarded as a rigid ring rotating about the Earth).

Ruelle’s proposal was formulated in the case of fluid mechanics: but it is so clearly more general that the reason why it was not explicitly proposed for statistical systems is probably due to the fact that, as a principle, it required some “check” if formulated for statistical mechanics: as originally stated and without any further check it would have been analogous, in my view, to the ergodic hypothesis without the heat theorem (or other consequences drawn from the theory of statistical ensembles).

Evidence for the nontrivial applicability of the hypoth-

esis built up quite rapidly and was repeatedly hinted at in various papers dealing with numerical experiments, mostly on very small particle systems ( $< 100$  to give an indication).<sup>5</sup> In attempting to understand one such experiment<sup>6</sup> the following “formal” interpretation of the Ruelle’s principle was formulated<sup>7</sup> for statistical mechanics (as well as for fluid mechanics, replacing “many particles system” with “turbulent fluid”) in the form:

*Chaotic hypothesis: A many particle system in a stationary state can be regarded as a transitive Anosov system (see below) for the purpose of computing the macroscopic properties of the system.*

The hypothesis was made first in the context of reversible systems (which were the subject of the experimental work that we were attempting to explain theoretically). The assumption that the system is Anosov (see below) has to be interpreted when the system has an attractor strictly smaller than the available phase space (i.e., not dense in it), as saying that the attractor itself can be regarded as a smooth Anosov systems (see below).

The latter interpretation *rules out* fractal attractors and, to include them, it could be replaced by changing “Anosov” into “Axiom A”: but I prefer to wait to see if there is a real need for such an extension. It is certainly an essential extension for small systems, but it is not clear how relevant fractality could be when the system has  $10^{23}$  particles.

A transitive Anosov system is a *smooth* system with a dense orbit (the latter condition is to exclude trivial cases, such as when the system consists of two chaotic but noninteracting subsystems) and when around every point  $x$  one can set up a local coordinate system that (a) *depends continuously on  $x$  and is covariant* (i.e., it follows  $x$  in its evolution) and (b) is *hyperbolic* (i.e., transversally to the phase space velocity of any chosen point  $x$  the motion of nearby points looks, when seen from the coordinate frame covariant with  $x$ , as a hyperbolic motion near a fixed point).

This means that on (each) plane transversal to the phase space velocity of  $x$  there will be a “stable coordinate surface,” the *stable manifold* through  $x$ , whose point trajectories get close to the trajectory of  $x$  at exponential speed as the time tends to  $+\infty$  and an “unstable coordinate surface,” the *unstable manifold*, whose trajectories get close to the trajectory of  $x$  at exponential speed as the time tends to  $-\infty$ . The direction parallel to the velocity can be regarded as a *neutral* direction where, on average, no expansion or contraction occurs.

Anosov systems are the *paradigm* of chaotic systems: they are the analogs of the harmonic oscillators for ordered motions. Their simple, but surprising and deep properties are, by and large, very well understood; particularly in the discrete time cases that we consider below. Unfortunately, they are not as well known as they should be among physicists, who seem confused by the language in which they are usually presented: however, it is a fact that such a remarkable mathematical object has been introduced by mathematicians and that physicists must therefore make an effort at understanding the new notion and its physical significance.

In particular, if a system is Anosov: *for all* observables  $F$  (i.e., continuous functions on phase space) and for almost

all initial data  $x$  the time average of  $F$  exists and can be computed by a phase space integral with respect to a distribution  $\mu$  uniquely determined on phase space  $\mathcal{F}$ :

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T F(S_t x) dt = \int_{\mathcal{F}} F(y) \mu(dy). \quad (8)$$

“Almost all” means apart from a set of zero volume in phase space. The distribution is called the SRB distribution: it was proven to exist by Sinai<sup>8</sup> for Anosov systems and the result was extended to the much more general Axiom A attractors by Ruelle and Bowen<sup>4</sup>. *Natural distributions* were, independently, discussed and shown to exist<sup>9</sup> for other (related and simpler) dynamical systems.

Clearly the chaotic hypothesis solves, *in general* (i.e., for systems that can be regarded as “chaotic”), the problem of determining which is the ensemble to use to study the statistics of stationary systems in or out of equilibrium (it clearly implies the ergodic hypothesis in equilibrium), in the same sense in which the ergodic hypothesis solves the equilibrium case.

Therefore the first problem with such a hypothesis is that it will be very hard to prove it in a mathematical sense: the same can be said about the ergodic hypothesis which is not only unproved for most cases, but will remain such, in systems of statistical mechanical interest, for a long time if not forever, aside from some very special cases (like hard core gas). The chaotic hypothesis might turn out to be false in interesting cases, like the ergodic hypothesis which does not hold for the simplest systems studied in statistical mechanics, like free gas, harmonic chain, and black body radiation. Worse, the chaotic hypothesis is *known* to be false for trivial reasons in some systems in equilibrium (like hard core gas), simply because the Anosov definition requires smoothness of the evolution and systems with collisions are not smooth systems (in the sense that the trajectories are not differentiable as functions of the initial data).

However, interestingly enough, the case of hard core systems is perhaps the system closest to an Anosov system that can be thought of and that is also of statistical mechanical relevance. To some extent, there seems to be no known properties that such a system does not share with an Anosov system. Aside from the trivial fact that it is not a smooth system, the hard core system behaves, for statistical mechanics purposes, *as if it was an Anosov system*. Hence it is the prototype system to study in looking for applications of the chaotic hypothesis.

The *problem* that remains is whether the chaotic hypothesis has any power to tell us something about nonequilibrium statistical mechanics. This is the real, deep, question for anyone, who is willing, to consider. *One consequence* is the ergodic hypothesis, hence the heat theorem, but this is *too little* even though it is a very important property for a theory with the ambition of being a *general* extension of the theory of equilibrium ensembles.

I conclude this section with a comment useful in the following. As is well known by whoever has attempted a numerical (or real) experiment, one does not often observe systems in continuous time: but rather one records the state

of the system at times when some event that is considered interesting or characteristic happens. Calling such events “*timing events*,” the system then appears to have a phase space of dimension one unit lower: because the set of timing events has to be thought of as a surface in phase space transversal to the phase space velocity of the trajectories  $t \rightarrow S_t x$ .

If  $x$  is a timing event and  $\vartheta(x)$  is the time that one has to wait until the next timing event happens, the time evolution becomes a map  $x \rightarrow Sx \equiv S_{\vartheta(x)}x$  of  $x$  into the following timing event. For instance, one could record the configuration of a system of hard balls every time a collision takes place, and  $S$  will map a collision configuration into the next one.

The chaotic hypothesis can be formulated for such “Poincaré’s sections” of a continuous time flow in exactly the same way: and this is, in fact, a simpler notion as there will be no “*neutral direction*” and the covariant local system of coordinates will be simply based on a stable and an unstable manifold through every point  $x$ .

In the following section we take the point of view that time evolution has been discretized in the above sense (i.e., via a Poincaré’s section on a surface of timing events): this simplifies the discussion, but in a minor way.<sup>10</sup>

### III. FLUCTUATION THEOREM FOR REVERSIBLY DISSIPATING SYSTEMS

The key to finding applications is that the apparently inconsequential hypothesis that the system is Anosov provides us with, not only with an existence theorem of the SRB distribution  $\mu$  but also with an explicit expression for it. How explicit? As we shall see, it is not too far from what we are used to in equilibrium statistical mechanics (e.g.,  $\mu = e^{-\beta H}$ ), where apparently unmanageable expressions and hopeless integrals have important and beautiful applications in spite of their obvious noncomputability.

Recalling that we are now considering a discrete time evolution  $S$ , as explained at the end of the preceding section, the expression is as follows: there is a partition of phase space into cells  $E_1, E_2, \dots$  which in a sense that I do not specify here<sup>11</sup> is “*covariant*” with respect to time evolution and to the other symmetries of the system (if any: think of parity or time reversal) such that the average value of an observable can be computed as

$$\langle F \rangle = \int_{\mathcal{F}} F(y) \mu(dy) = \frac{\sum_{E_i} \Lambda_{u,T}^{-1}(x_i) F(x_i)}{\sum_{E_i} \Lambda_{u,T}^{-1}(x_i)}, \quad (9)$$

where  $x_i \in E_i$  is a point suitably chosen in  $E_i$  (quite, but not completely, arbitrarily for technical and trivial reasons<sup>7,11</sup>) and  $\Lambda_{u,T}(x)$  is the expansion of a surface element lying on the unstable manifold of  $S_{-(1/2)T}x$  and mapped by  $S_T$  into a surface element around  $S_{(1/2)T}x$ .

Of course Eq. (9) requires that the cells be so small that  $F$  has negligible variations inside them: if this is not the case, then one simply has to *refine* the partition into smaller cells, until they become so small that  $F$  is a constant inside them (for practical purposes). This can be done by simply applying the time evolution map and its inverse to the partition  $\mathcal{E}$  that we already imagine having, but which has large cells, and then intersecting the elements of the new partitions ob-

tained, to get a finer partition. Concretely, we can take the partition obtained by intersecting the elements of the partitions  $S^j \mathcal{E}$ ,  $-T \leq j \leq T$ , and by taking  $T$  large enough: in this way we link  $T$  to the size of the partition cells and Eq. (9) becomes exact in the limit as  $T \rightarrow \infty$ . The hyperbolicity of the evolution implies that the partition into cells can be made as fine as desired. The above method of refining a partition is suggested by the fact that such refinements *preserve the covariance and symmetry properties* mentioned above, necessary for Eq. (9) to have a chance to hold.<sup>7,11</sup>

Another reason we need small cells is to insure that the weights themselves do not depend too much on which point  $x_i$  is chosen to evaluate them: the precise condition is somewhat delicate.<sup>12</sup>

An example of an application of the above formula is obtained by studying the phase space volume contraction rate  $\sigma(x)$ : this is defined as minus the logarithm of the Jacobian determinant  $\Lambda(x)$  of the time evolution map. Suppose that we ask for the fluctuations of the average of the “dimensionless contraction”  $\sigma(x)/\sigma_+$ , where  $\sigma_+$  is the (infinite) time average  $\sigma_+ = \int \sigma(y) \mu(dy)$ , that is assumed strictly positive (it could be zero, for instance, in a equilibrium system where the evolution is Hamiltonian and conserves volume in phase space; but it cannot<sup>13</sup> be  $< 0$ ). The positivity of the time average of  $\sigma$  can be taken as the very definition of “*dissipative*” motions.

The quantity  $p = (1/\tau\sigma_+) \sum_{k=-\tau}^{(1/2)\tau} \sigma(S^k x)$  is the average in question and it will have a probability distribution, in the stationary state, that we write  $\pi_\tau(p)$ . We now compare  $\pi_\tau(p)$  to  $\pi_\tau(-p)$ , which is clearly a ratio of probabilities of two events, one of which will have an extremely small probability (the expected value of  $p$  being 1).

Suppose that the system is time reversible: i.e., that there is an isometry of phase space  $I$  that anticommutes with the evolution:  $IS = S^{-1}I$ . Then

$$\frac{\pi_\tau(p)}{\pi_\tau(-p)} = \frac{\sum_{E_i: p} \Lambda_{u,T}^{-1}(x_i)}{\sum_{E_i: -p} \Lambda_{u,T}^{-1}(x_i)}, \quad (10)$$

where the sum in the numerator extends over the cells  $E_i$  in which the total dimensionless volume contraction rate is  $p$  and the sum in the denominator over those with contraction rate  $-p$ .

Here we take  $T = \tau$  for the purpose of a partial illustration: this is *not* allowed and in a sense it is the *only* difficulty in the discussion. But taking  $T = \tau$  conveys some of the main ideas. If this “interchange of limits” is done, then one simply notes that the sum in the denominator of Eq. (10) can be performed over the same cells as that in the numerator, provided we evaluate the weight in the denominator at the point  $Ix_i$ , i.e., provided we use the weight  $\Lambda_{u,T}^{-1}(Ix_i)$  in the denominator: this is so because time reversal maps a cell in which the dimensionless rate of volume contraction is  $p$  into one in which it is  $-p$  and vice versa. However, time reversal also interchanges expansion and contraction so that  $\Lambda_{u,T}^{-1}(Ix_i) = \Lambda_{s,T}(x_i)$ , if the contraction rate along the stable manifold  $\Lambda_{s,T}$  is defined in the same way as  $\Lambda_{u,T}$  by exchanging stable and unstable manifolds. This means that the ratio between corresponding terms is now  $\Lambda_{u,T}^{-1}(x_i) \Lambda_{s,T}^{-1}(x_i)$ .

Since the latter quantity is essentially the *total contraction rate* up to a factor bounded independently of the value of  $T$  (because the angle between the stable and unstable manifolds is bounded away from zero by the continuity property of Anosov systems) it follows that the ratio Eq. (10), in this (rather uncontrolled) approximation  $T = \tau$ , is  $\tau p \sigma_+$ , i.e., simply the contraction rate which has the *same value for all cells considered*, by construction. Conclusion:

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau p \sigma_+} \log \frac{\pi_\tau(p)}{\pi_\tau(-p)} = 1, \quad (11)$$

which is the *fluctuation theorem* if  $\pi_\tau$  are evaluated with respect to the SRB distribution of the system.

The above “proof” is missing a key point: namely the interchange of limits. Fixing  $\tau = T$  means that we are not computing the probabilities in the SRB distribution but, at best, in some approximation of it. In experimental tests one needs the theorem to hold when the limits are taken in the proper order (i.e., first  $T \rightarrow \infty$  and then  $\tau \rightarrow \infty$ ). The latter theoretical aspects have been discussed in the original papers,<sup>7</sup> where it is shown that the limit is approached as  $\tau^{-1}$ ; and formal proofs are also available.<sup>14,15</sup>

That this is not a fine point of rigor can be seen from the fact that if one disregards it then other proofs of the “same” result but with  $\tau = T$  become possible. In other words the result has a “tendency” to be general<sup>16,17</sup> but it can be proved in the right form of Eq. (11) only under strong chaoticity assumptions. It is very interesting that in weaker forms a result closely related to the fluctuation theorem can be obtained for *completely different* dynamical systems, i.e., for stochastic evolutions.<sup>17</sup> It is possible that for the stochastic evolution the result could be extended to become a closer analog of the above, solving the mentioned problem of the interchange of limits: one would, in fact, think that the noise makes the system as chaotic as one may possibly hope.

The result, Eq. (11), has to be tested because in all applications we do not know whether the system is Anosov and to what extent it can be assumed to be such. Its verification provides a form of test of the chaotic hypothesis.

Other equivalent formulations of the fluctuation theorem are in terms of the “free energy” of the observable  $p$ :  $\zeta(p) = \lim_{\tau \rightarrow \infty} 1/\tau \log \pi_\tau(p)$ ; it becomes

$$\frac{\zeta(p) - \zeta(-p)}{p \sigma_+} = 1, \quad (12)$$

which says that the odd part of  $\zeta(p)$  is linear in  $p$  with a *determined and parameter free* slope: note that without reversibility one could only expect that  $\zeta(p)$  had a quadratic maximum at  $p = 1$  [central limit theorem for the observable  $\sigma(x)$ ] which stays quadratic as long as  $|p - 1| = O(1/\sqrt{\tau})$ . The fluctuation theorem instead gives information concerning huge deviations  $|p - 1| = O(2)!$ , it is a *large deviation theorem*.

The main interest, so far, of the above theorem is that it has shown that Ruelle’s principle has some power of prediction. In fact the result has been checked in various small

systems.<sup>18</sup> The first of which was its experimental discovery<sup>6</sup> preceding the chaotic hypothesis and fluctuation theorem formulations.

It is also interesting because of its *universal validity*: it is system independent (provided reversible), hence it is a general law that should be satisfied if the chaotic hypothesis is the correct mathematical translation of our intuitive notion of chaos, and Anosov systems catch it fully.

The question whether the above results can also be obtained from the chaotic hypothesis formulated in terms of the continuous time flow on phase space (rather than for a map between timing events, see the last comments in the previous section) would leave us unhappy if it did not have a positive answer: it does have a positive answer.<sup>10</sup>

#### IV. ONSAGER’S RECIPROCITY AND GREEN-KUBO’S FORMULA

The fluctuation theorem degenerates in the limit in which  $\sigma_+$  tends to zero, i.e., when the external forces vanish and dissipation disappears (and the stationary state becomes the equilibrium state).

Since the theorem deals with systems that are time reversible *at and outside* equilibrium Onsager’s hypotheses are certainly verified and the system should obey reciprocal response relations at vanishing forcing. This led to the idea that there might be a connection between fluctuation theorem and Onsager’s reciprocity and also to the related (stronger) Green-Kubo’s formula.

This is, in fact, true: if we define the *microscopic thermodynamic flux*  $j(x)$  associated with the *thermodynamic force*  $E$  that generates it, i.e., the parameter that measures the strength of the forcing (which makes the system not Hamiltonian), via the relation

$$j(x) = \frac{\partial \sigma(x)}{\partial E} \quad (13)$$

(not necessarily at  $E = 0$ ), then in Ref. 14 a heuristic proof shows that the limit as  $E \rightarrow 0$  of the fluctuation theorem becomes simply (in the continuous time case) a property of the average, or “macroscopic,” flux  $J = \langle j \rangle_{\mu_E}$ :

$$\frac{\partial J}{\partial E} \Big|_{E=0} = \frac{1}{2} \int_{-\infty}^{\infty} \langle j(S_t x) j(x) \rangle_{\mu_E} \Big|_{E=0} dt, \quad (14)$$

where  $\langle \cdot \rangle_{\mu_E}$  denotes average in the stationary state  $\mu_E$  (i.e., the SRB distribution which, at  $E = 0$ , is simply the microcanonical ensemble).

If there are several fields  $E_1, E_2, \dots$ , acting on the system we can define several thermodynamic fluxes

$$\stackrel{\text{def}}{j_k}(x) = \partial_{E_k} \sigma(x)$$

and their averages  $\langle j_k \rangle_{\mu}$ : a simple extension of the fluctuation theorem<sup>19</sup> is shown to reduce, in the limit in which all forces  $E_k$  vanish, to

$$L_{hk} = \frac{\partial J_h}{\partial E_k} \Big|_{E=0} = \frac{1}{2} \int_{-\infty}^{\infty} \langle j_h(S_t x) j_k(x) \rangle_{E=0} dt = L_{kh}, \quad (15)$$

therefore we see that the fluctuation theorem can be regarded as an extension to nonzero forcing of Onsager's reciprocity and actually, of Green-Kubo's formula.

Certainly assuming reversibility in a system out of equilibrium can be disturbing: therefore one can ask if there is a more general connection between the chaotic hypothesis and Onsager's reciprocity and Green-Kubo's formula. This is indeed the case and provides us with a *second application* of the chaotic hypothesis valid, however, only in zero field. It can be shown that the relations in Eq. (15) follow from the sole assumption that at  $E=0$  the system is time reversible and that it verifies the chaotic hypothesis at  $E=0$ : at  $E \neq 0$  it can be, as in Onsager's theory, not reversible.<sup>20</sup>

It is not difficult to see, technically, how the fluctuation theorem, in the limit in which the driving forces tend to 0, formally yields Green-Kubo's formula.

We consider time evolution in continuous time and simply note that Eq. (11) implies that, for all  $E$  (for which the system is chaotic),

$$\lim_{\tau \rightarrow \infty} \frac{1}{\tau} \log \langle e^{I_E} \rangle_{\mu_E} = 0, \quad (16)$$

where

$$I_E \stackrel{\text{def}}{=} \int_{-\pi/2}^{\pi/2} \sigma(S_t x) dt$$

with  $\sigma(x)$  being the divergence of the equations of motion (i.e., the phase space contraction rate, in the case of continuous time). This remark<sup>21</sup> [that says that essentially  $\langle e^{I_E} \rangle_{\mu_E} \equiv 1$  or more precisely it is not too far from 1 so that Eq. (16) holds] can be used to simplify the analysis in Ref. 19 as follows.

Differentiating both sides with respect to  $E$ , not worrying about interchanging derivatives, limits, and the like, one finds that the second derivative with respect to  $E$  is a sum of six terms. Supposing that for  $E=0$  the system is Hamiltonian and (hence)  $I_0 \equiv 0$ , the six terms are, when evaluated at  $E=0$ :

$$\begin{aligned} & \frac{1}{\tau} \langle \partial_E^2 I_E \rangle_{\mu_E} \Big|_{E=0} - \frac{1}{\tau} \langle (\partial_E I_E)^2 \rangle_{\mu_E} \Big|_{E=0} \\ & + \frac{1}{\tau} \int \partial_E I_E(x) \partial_E \mu_E(x) \Big|_{E=0} \\ & - \frac{1}{\tau} \left( \langle (\partial_E I_E)^2 \rangle_{\mu_E} \cdot \int 1 \partial_E \mu_E \right) \Big|_{E=0} \\ & + \frac{1}{\tau} \int \partial_E I_E(x) \partial_E \mu_E(x) \Big|_{E=0} + \frac{1}{\tau} \int 1 \cdot \partial_E^2 \mu_E \Big|_{E=0} \end{aligned} \quad (17)$$

and we see that the fourth and sixth terms vanish being derivatives of  $\int \mu_E(dx) \equiv 1$ , the first vanishes (by integration by parts) because  $I_E$  is a divergence and  $\mu_0$  is the Liouville distribution (by the assumption that the system is Hamiltonian at  $E=0$  and chaotic). Hence we are left with

$$\left( -\frac{1}{\tau} \langle (\partial_E I_E)^2 \rangle_{\mu_E} + \frac{2}{\tau} \int \partial_E I_E(x) \partial_E \mu_E(x) \right) \Big|_{E=0} = 0, \quad (18)$$

where the second term is, since the distribution  $\mu_E$  is stationary,  $2\tau^{-1} \partial_E \langle (\partial_E I_E) \rangle_{\mu_E} \Big|_{E=0} \equiv 2 \partial_E J_E \Big|_{E=0}$ ; and the first term tends to  $\int_{-\infty}^{+\infty} \langle j(S_t x) j(x) \rangle_{E=0} dt$  as  $\tau \rightarrow \infty$ . Hence we get Green-Kubo's formula in the case of only one forcing parameter.

The argument should be extended to the case in which  $E$  is a vector describing the strength of various driving forces acting on the system:<sup>19</sup> but one needs a generalization of Eq. (16). The latter is a consequence of the fluctuation theorem, but the theorem had to be extended<sup>19</sup> to derive also Green-Kubo's formula (hence reciprocity) when there were several independent forces acting on the system.

The above analysis is unsatisfactory because we interchange limits and derivatives quite freely and we even take derivatives of  $\mu_E$ , which seem to require some imagination as  $\mu_E$  is concentrated on a set of zero volume. On the other hand, under the strong hypotheses in which we suppose that the system is Anosov, we should not need extra assumptions. Indeed the above mentioned nonheuristic analysis<sup>20</sup> is based on the study of the differentiability of SRB distributions with respect to parameters.<sup>22</sup>

A *third application* of the chaotic hypothesis, still limited to reversible systems, is the following: consider the probability that certain observables  $O_1, O_2, \dots$  are measured during a time interval  $[-\frac{1}{2}\tau, \frac{1}{2}\tau]$  during which the system evolves between the point  $S_{-1/2\tau}x$  and  $S_{1/2\tau}x$ . And suppose that we see the *path* or *pattern*  $\omega$  given by  $t \rightarrow O_1(S_t x), O_2(S_t x), \dots$

Assuming, for simplicity, that  $O_j$  are *even* under time reversal the "time reversed" pattern  $I\omega$  will be  $t \rightarrow O_1(S_{-t}x), O_2(S_{-t}x)$  and it will be, clearly, *very unlikely*. Suppose that we look at the relative probabilities of various patterns *conditioned* to an average (over the time interval  $[-\frac{1}{2}\tau, \frac{1}{2}\tau]$ ) dimensionless volume contraction rate  $p$ . Then one can prove,<sup>23</sup> under the chaotic hypothesis, that the relative probabilities of patterns in the presence of rate  $p$  is the same as that of the time reversed patterns in the presence of rate  $-p$ .

Since the contraction rate of volume in phase space can be interpreted as the *entropy creation rate*, as suggested, for instance by the above use of, see Eq. (4) of the phase space contraction to define the thermodynamic fluxes, as "conjugate" observables to the external thermodynamic forces, the latter statement has some interest as it can be read to say that "it costs no extra effort to realize events normally regarded as impossible once one succeeds in the enterprise of reversing the sign of entropy creation rate."<sup>23</sup>

The interpretation of phase space contraction rate as *entropy creation rate* meets opposition, fierce at times: however, it seems a very reasonable proposal for a concept that we should not forget has not yet received a universally accepted definition and therefore its definition should at least be considered as an open problem.

## V. REVERSIBLE VERSUS IRREVERSIBLE DISSIPATION. NONEQUILIBRIUM ENSEMBLES?

A system driven out of equilibrium can reach a stationary state (and not steam out of sight) only if enough dissipation is present. This means that any mechanical model of a

system reaching a stationary state out of equilibrium *must* be a model with nonconservative equations of motion in which forces representing action of thermostats, that keep the system from heating up, are present.

Thus a generic model of a system stationarily driven out of equilibrium will be obtained by adding to Hamilton's equations (corresponding to the nondriven system) other terms representing forces due to the thermostat action.

Here one should avoid attributing a fundamental role to special assumptions about such forces. One has to realize that there is *no privileged* thermostat. One can consider many of them and they simply describe various ways to take out energy from the system.

Thus one can use stochastic thermostats, and there are many types considered in the literature; or one can consider deterministic thermostats and, among them, reversible ones or irreversible ones.

Each thermostat requires its own theory. However, the same system may behave in the same way under the action of different thermostating mechanisms: if the only action we make on a gas tube is to keep the temperatures fixed at the extremes by taking heat in or out of them, the difference may be irrelevant, at least in the limit to which the tube becomes long enough, as far as what happens in the middle of it is concerned.

But of course the form of the stationary state may be very different in the various cases, even when we think that the differences are only minor boundary effects. For instance, in the case of the gas tube, if our model is of deterministic dissipation we expect the SRB state to be concentrated on a set of *zero phase space volume* (because phase space will in the average contract, when  $\sigma_+ > 0$ , so that any stationary state has to be concentrated on a set of zero volume, which, however, could still be dense and usually will be). While, if the model is stochastic then the stationary state will be described by a *density* on phase space. Nothing could seem more different.

Nevertheless, it might be still true that in the limit of an infinite tube that the two models give the same result: in the same sense as the canonical and microcanonical ensembles describe the same state even though the microcanonical ensemble is supported on the energy surface, which has zero volume if measured by using the canonical ensemble (which is given by a density over the whole available phase space).

Therefore we see that out of equilibrium we have in fact *much more freedom to define equivalent ensembles*. Not only do we have (very likely) the same freedom that we have in equilibrium (like fixing the total energy or not, or fixing the number of particles or not, passing from microcanonical to canonical to grand canonical, etc.) but *we can also change the equations of motion and obtain different stationary states, i.e., different SRB distributions, which will, however, become the same in the thermodynamic limit*.

Being able to prove the mathematical equivalence of two thermostats will amount at proving their physical equivalence. This again will be a difficult task, in any concrete case.

What I find fascinating is that the above remarks provide us with the possibility that a *reversible thermostat can be equivalent in the thermodynamic limit to an irreversible one*.

I conclude by reformulating a conjecture that I have already stated many times in talks and articles,<sup>24</sup> which clarifies the latter statement.

Consider the following two models describing a system of hard balls in a periodic (large) box in which there is a lattice of obstacles that forbid collisionless paths (by their arrangement and size): the laws of motion will be Newton's (elastic collisions with the obstacles as well as between particles) plus a constant force  $E$  along the  $x$ -axis *plus a thermostating force*.

In the first model, the thermostating force is simply a constant times the momentum of the particles: it acts on the  $i$ th particle as  $-\nu p_i$  if  $\nu$  is a "friction" constant. Another model is a force proportional to the momentum but via a proportionality factor that is not constant and depends on the system configuration: it has the form  $-\alpha(x)p_i$  with  $\alpha(x) = E \cdot \sum_i p_i / \sum_i p_i^2$ .

The first model is essentially the model used by Drude in his theory of conduction in metals. The second model has been used very often in recent years for theoretical studies and has thus acquired a respected status and a special importance: it was among the first models used in the experiments and theoretical ideas that led to the connection between Ruelle's ideas for turbulent motion in fluids and nonequilibrium statistical mechanics.<sup>5</sup> I think that the importance of such works should be clearly recognized: without them the recent theoretical developments would have been simply unthinkable, in spite of the fact that *a posteriori* they seem quite independent and one could claim (unreasonably in my view) that everything could have been done much earlier.

Furthermore the second model can be seen as derived from Gauss' least constraint principle. It keeps the total (kinetic) energy exactly constant over time (taking energy in and out, as needed) and is called *Gaussian thermostat*. *Unlike the first model it is reversible*, with time reversal being the usual velocity inversion. Thus the above theory and results based on the chaotic hypothesis apply.

My conjecture was (and is) that:

(1) Compute the average energy per particle that the system has in the constant friction case and call it  $\mathcal{E}(\nu)$  calling also  $\mu_\nu$  the corresponding SRB distribution.

(2) Call  $\tilde{\mu}_\mathcal{E}$  the SRB distribution for the Gaussian thermostat system when the total (kinetic) energy is fixed to the value  $\mathcal{E}$ .

(3) Then  $\mu_\nu = \tilde{\mu}_{\mathcal{E}(\nu)}$  *in the thermodynamic limit* (in which the box size tends to become infinitely large but with the number of particles and the total energy correspondingly growing so that one keeps the density and the energy density constant) and for *local* observables, i.e., for observables that depend only on the particles of the system localized in a fixed finite region of the container. This means that the equality takes place in the usual sense of the theory of ensembles.<sup>25</sup>

This opens the way to several speculations as it shows that the reversibility assumption might not be so strong after all. And results for reversible systems may carry through to irreversible ones.

I attempted to extend the above ideas also to turbulent motions but I can only give here Refs. 24 and 26. In the latter



papers, following the developments in Refs. 18 and 27 it is suggested that the fluctuation theorem can be extended to strongly dissipative systems for which the attracting set has a closure smaller than phase space at the price of a change in slope from the 1 in Eq. (12) to a value  $\bar{P} < 1$  depending on the Lyapunov exponents of the motions. This may be relevant in the interpretation of recent experimental results.<sup>28</sup>

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