

Appendix: Nonequilibrium thermodynamics ? twentyseven comments

Here one of us (Gi.G.) adds a few (personal) comments on the physical meaning of entropy which appeared in november 2002, stimulated by continuous heated discussions held at Rutgers University in the course of the last few years: involving, among many others, in particular S.Goldstein, J.Lebowitz, D.Ruelle. The twenty-seven comments (marked by a \bullet) on the Second Law and nonequilibrium systems are related particularly to the contents of Chapter X and give a very personal (and apparently controversial) outlook on the role of entropy in nonequilibrium thermodynamics. Appropriate extensions of the SRB distributions, cf. definition (6.2.2), seem to be the correct generalization of the equilibrium distributions (Gibbs distributions) to describe the statistics of the motions of *stationary* nonequilibrium states: here the view is held that attempting an extension of the definition of *entropy* to stationary nonequilibrium systems may not be the right direction to proceed. The discussion that follows suggests that the connection between the entropy notion that is useful in ergodic theory and information theory (as employed in this book) may be related to entropy in macroscopic Thermodynamics in a subtle way: and possibly not really identifiable with it. The problem becomes particularly evident when one tries to extend entropy to nonequilibrium Thermodynamics understood as the study of general properties of transformations in which a system evolves through a sequence of *stationary* states (while classical Thermodynamics deals with evolutions through sequences of equilibrium states). A stationary state can be an equilibrium state, when the system is controlled by conservative forces, or a nonequilibrium state, when the system is subject to nonconservative forces and can reach a stationary state only if the work done by the external forces is appropriately dissipated by “thermostats”: as in the case of a constant electromotive field on closed conducting wire. In the following discussion one should carefully distinguish between the transient phenomena that occur while a system approaches a stationary state and the phenomena associated with the stationary state itself: the distinction is exemplified by an analysis of the Joule’s expanding gas experiment.

Definitions.

The purpose, in the present discussion, is investigating the possibility of an extension of Thermodynamics to systems which are in a stationary state but are subject to the action of conservative and nonconservative positional forces f_{-pos} and (therefore) also to the action of the forces $\underline{\varrho}$ necessary to

take away the heat thus generated.

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

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

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

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

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

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

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

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¹ This means that “typical” is any initial state chosen with a probability distribution absolutely continuous with respect to the volume on phase space. This is not to be taken for granted, even though it is very often considered so: here I do not enter into discussing this mysterious assumption (as I have nothing to say). For instance an initial state chosen with a probability distribution which is uniform on the energy surface of energy U of a system that occupies half of a volume V is typical for the gas enclosed in the full box V because the configurations which occupy half the box have positive probability among the ones allowed to occupy the full box: see below. Of course the statistics of the configurations just considered is completely different if there is a physical wall separating the two halves of the box or if it is absent.

(typical) point in phase space, like of its “entropy”, we always mean the same property of the equilibrium state for which the datum is a typical one.

Remarks: This already might be controversial: in fact the above (admittedly unconventional) definition of entropy has the following implications. A rarefied gas which initially happens to have all molecules located in the left half of a container, because a separation wall has just been removed, setting the gas in macroscopic motion and out of the previous equilibrium state, will be an initial datum in phase space whose entropy is that of the same gas occupying the entire container and at the same temperature² (the difference residing only in the different dynamics that follows the removal the wall in the middle of the container). Since a physicist would apply the Boltzmann equation to describe the evolution, the question arises about which is the place here of Boltzmann’s H -function, which is different if evaluated for the initial datum or for a datum into which the initial one evolves after a moderately large time (and in both cases it equals the classical thermodynamic entropy of the initial and final equilibria).

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(•) In trying to study nonequilibrium cases a conceptual difficulty must be met: if a system is subject to external non conservative forces then the thermostating forces will have a non zero divergence and volume in phase space will not be preserved. The key idea (due to Ruelle) [Ru95] is that in this case (extending, and including, the previous case) the nonequilibrium states will be the stationary states which are generated by time averaging of initial states that have a density or more satisfactorily, perhaps, by time averaging on the evolution of initial data that are typical for probability distributions given by some (arbitrary) density. The latter states are called *SRB distributions* (Sinai,Ruelle,Bowen, [Ru95],[Ru99],[Ga00],[Ga02]). Their appearance is natural since there will be *no state* (*i.e.* no probability distribution) which is stationary and at the same time is also given by a density. As in the equilibrium state we shall attribute to each individual point in phase space the macroscopic properties of the stationary state which allows us to compute the averages of macroscopic observables on the motion of the given point.

Remark: Systems that are chaotic in a mathematical sense (*hyperbolic systems*) can be shown, on rather general grounds, to have the property that there is only one SRB distribution (with the correct values of the macroscopic parameters), [Ru95],[Ru99],[Ga02]. Therefore such systems, the only ones for which the above definition has a strict mathematical sharpness, verify an extension of the ergodic hypothesis: adopting the latter definition means believing that the system is *chaotic enough* so that typical initial data generate a unique stationary distribution with several features of the

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

SRB distributions for hyperbolic systems: the assumption has been called *chaotic hypothesis*, [GC95], and it represents (in our analysis) the nonequilibrium analogue of the classical ergodic hypothesis.

(●) Given an initial state (a typical point or a distribution on phase space) it might be possible to define a function of it that, at least if the state is evolved with an equation which is a good approximation for very long times, will monotonically increase to a limit value which is the same for almost all data sampled with a distribution with a density on phase space (*i.e.* absolutely continuous). Since Boltzmann’s H -function is an example of such a function we shall call H -functions all such functions: among them one should also mention the “*Resibois’ H function*” for systems described by Enskog’s equation (hard sphere systems) and the “(*Boltzmann*) *entropy*” for systems in local thermal equilibrium [Re78],[GL03]. We recall that Boltzmann’s H -function is defined by a coarse graining of phase space into “macrostates” determined by the occupation numbers $f(p, q)d^3pd^3q$ of phase space cells d^3pd^3q around p, q and by defining $H = - \int f(p, q) \log f(p, q) d^3pd^3q$. Clearly here the cells size affects by an additive constant the actual value of H , which therefore should have no significance (at least in the classical mechanics context in which we are working) and only the variations of H can be meaningful. In a rarefied gas the Boltzmann equation applies approximately (and even exactly within the Grad’s approximation, [Ga00]): so that in the latter cases the function just defined is a nontrivial example of an H -function. See also [Ru03].

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

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³ One should note that in the whole Boltzmann’s work he has been really concerned with the approach to equilibrium: in our terminology he has been concerned with the problem of determining the stationary equilibrium distribution to which a given initial datum gives rise at large time: restricting consideration only to such cases one could well call the Boltzmann’s H -function the “entropy” of the state as it evolves towards equilibrium. And, whatever name we give it, it remains true that H is a measure of the disorder in the system. Our analysis here is intended to say that such an interpretation

(•) The latter property could possibly be used to attempt a definition of entropy for states which are neither equilibrium nor stationary states, [Le93] however such a definition would be useful only in the special situations in which an H -theorem could be proved. That seems effectively to reduce the cases in which the notion would be useful to the ones in which an initial equilibrium state identified by some parameters (like U, V) evolves towards a final one identified by other values of the parameters. And even in such cases it is severely restricted to the rarefied gases evolutions in which the H -theorem can be proved: a proposed model independent, universal, extension of the above H -function would have to be proved to have a monotonicity property, at least at a heuristic level and within approximations in which exceedingly long times are involved, to avoid that its assumed monotonicity becomes an *a priori* law of nature.

(•) In general I would think that there will always be a Lyapunov function which describes the evolution of an initial state and is maximal on the stationary state that its evolution will eventually reach: however such a Lyapunov function may not have a universal form (unlike the H -function in the rarefied gases cases) and it may depend on the particular way the system is driven by the external forces. After all the SRB distribution verifies, cf. Section §6.2, a variational principle (Ruelle), [Ru95],[Ru99],[Ga02], which *remarkably* has the same form both in equilibrium and nonequilibrium systems and one may imagine that in general it will be possible to define (on a case by case basis, I am afraid) a quantity that, within a good approximation, will tend in a short time to a maximum reached on the eventual stationary state. This picture seems to me simpler than trying to guess a (possibly nonexistent) general definition of a quantity that would play the role of Boltzmann's H .

Entropy creation.

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

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

Of course this will be assumed to be a law of nature (Clausius), [Ze68].

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

is not tenable when the system evolves towards a stationary nonequilibrium state. It must also to be said that even the H -theorem is *not general* because it applies only to rarefied gases, and even there it is an approximation (in which exceedingly long times are not considered): to extend it to general situations, even when one only deals with approach to equilibrium, is a profound statement which should be substantiated by appropriate arguments.

$$S_2 - S_1 \geq \int_1^2 \frac{dQ}{T}$$

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

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

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

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

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

where $\sigma_t \stackrel{def}{=} \langle \sigma(\underline{x}, \dot{\underline{x}}) \rangle_{\mu^{(t)}}$ is the average phase space contraction computed in the state $\mu^{(t)}$. This follows a recently proposed identification of $\sigma(\underline{x}, \dot{\underline{x}})$ as proportional to the *entropy creation rate* (here c is a proportionality constant), [EM90]. The quantity Δ is for mechanical thermostats the analogue of $-\int_1^2 \frac{dQ}{T}$ for the generic phenomenological thermostats characterized by a temperature T .

⁴ Which in a sense is tantamount of asking “is there a nonequilibrium Thermodynamics?”

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(•) In considering macroscopic systems one may imagine situations in which a system is partially thermostatted by mechanical forces for which a model considered physically reasonable is available⁵ and partially by phenomenologically defined “heat reservoirs” characterized by a temperature T and able to cede to the system quantities dQ of heat (dQ can have either sign or vanish).

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

$$-\Delta + \int_1^2 \frac{dQ}{T} \leq 0$$

assuming that the cyclic path leading from 1 to 2 consists entirely of nonequilibrium stationary states and that it lasts a time interval $[0, \Theta]$ (i.e. 1 and 2 differ only because their times are different). Regarding the external thermostats as thermodynamic equilibrium systems $-\frac{dQ}{T}$ is the entropy increase of the reservoirs at temperature T and $\Delta = c \int \langle \sigma \rangle_t$ is interpreted as the entropy increase of the mechanical reservoir: if this interpretation is accepted the above relation becomes the ordinary second law for the external reservoirs and could be read as “the entropy of the rest of the universe does not decrease” (because $\Delta - \int_1^2 \frac{dQ}{T} \geq 0$), where “universe” is not the astronomical Universe but rather the collection of physical systems whose interaction with the system under study cannot be neglected.

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

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(•) Since the quantity σ_t is ≥ 0 (Ruelle), [Ru99], under very general conditions (in fact always if the chaotic hypothesis is assumed to hold true) $\Delta \geq 0$ and the proposed extension is compatible with the main consequences of the second law. The constant c will be taken 1 because the factor 1 can be computed by studying the expression of $\sigma(\underline{x}, \dot{\underline{x}})$ in special models: at the moment, however, I see no immediate physical implications of the “universality” of this choice of c and for the purposes of what follows c could be any constant, even non universal.

(•) The above implies again that we shall *not* be able to define an entropy function *unless* $\sigma_t \equiv 0$. The latter is the condition under which equilibrium

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

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

Thermodynamics is set up: so that if one studies only transformations from equilibrium states to other equilibrium states it is possible to define not only the creation of entropy but the entropy itself (up to an additive constant). In other words *transformations between equilibrium states play the role for entropy that isochoric transformations play for heat*: if we only consider adiabatic transformations between equilibrium states then heat is a function of state, likewise if we restrict to equilibrium states then entropy is a function of state; for more general (stationary) states and their transformations neither is a function of state but still it makes sense to talk about their creation.

(•) A number of compatibility questions arise: suppose that the system evolves between 1 and 2 under the action of a thermostat which is modeled by forces that act on the system. For instance we can imagine a container with periodic boundary conditions, we call it a *closed wire*, containing a lattice of obstacles, which we call a *crystal*, and N particles, which we call *electrons*, interacting between each other and with the lattice via hard core interactions (say) and subject also to a constant force, which we call *electromotive force*, of intensity E ; furthermore the particles will be subject to a thermostat force of Gaussian type⁷ (as it is essentially the case in Drude's theory as described in classical electromagnetism treatises, [Be64]) which forces the particles to have an energy $U = u(E)$ which is an assigned function of E . Suppose that the value of E changes in time (very slowly compared to the microscopic time scales) following a profile $E(t)$ as drawn in Fig.1

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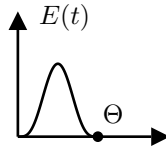


Fig.A1

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

(•) *It is* (perhaps) *natural to define the “temperature” of a mechanical thermostat* by remarking that in the models studied in the literature it turns out that σ_t is proportional to the work per unit time that the mechanical forces perform, the proportionality constant being in general a function of the point in phase space. Therefore we can call T_0^{-1} the time average of the proportionality constant between σ and the work W per unit time that the mechanical thermostating forces perform: in this way $\sigma_t = \frac{W}{T_0}$ and $\int_0^\Theta \sigma_t dt = \int \frac{dQ_0}{T_0}$ where dQ_0 is the total work performed by the mechanical forces *which we can* (naturally) *call the heat absorbed by the mechanical*

⁷ This is not the appropriate place to remind the Gauss' least constraint principle: it can be easily found in the literature, [Ga00].

reservoir.

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

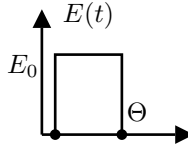


Fig.A2

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

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

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

Mechanical and stochastic models.

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

In this case the whole matter was originated by efforts to interpret results that started to appear in the late 1970's concerning numerical experiments in molecular dynamics, [EM90].

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

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

generators that one has to use and which, as it is well known, are simply suitably chaotic dynamical systems themselves).

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

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

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

(●) In my view it is likely that vast classes of thermostats, deterministic and stochastic as well, are equivalent in the sense that they produce motions which although very different when compared at equal initial conditions and at each time have, nevertheless, the same statistical properties, [Ga00],[Ga02]. And in my opinion there is already evidence that it is indeed possible to simulate the same system with simple deterministic thermostats or with some corresponding stochastic ones.

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

One among the most striking examples of such equivalence (She,Jackson), [SJ93], is the equivalence between the dissipative Navier–Stokes fluid and the Euler fluid in which the energy content of each shell of wave numbers is fixed (via Gauss’ least constraint principle) to be equal to the value that Kolmogorov’s theory predicts to be the energy content of each shell at a given (large) Reynolds number. Here one compares two very different mechanical thermostats. A more general view on the equivalence between different

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

thermostats has been developed since. In fact many instances in which Physicists say that “an approximation is reasonable” really correspond to equivalence statements about certain properties of different theories (and in the best cases the statements can be translated into proper mathematical conjectures).

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

A collision between the previously held views, masterfully summarized by the book of De Groot–Mazur, [DGM84], based on *continuum mechanics* and the new approaches based on *transistors, chips and dynamical systems theory* ensued: often showing that the two communities give the impression of not really meditating on each other arguments.

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

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

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

This is a *parameter free* symmetry relation that was discovered in a numerical experiment (Evans, Cohen, Morriss), [ECM93], and which has been checked in many cases. By very chaotic one means that the motion of the system can be assimilated to that of a suitable Anosov flow whose trajectories fill densely phase space (transitive Anosov flow).

(●) Indeed for transitive reversible Anosov systems the above relation holds as a theorem, [GC95]. Since models of physical systems are *not* Anosov systems from a strict mathematical point of view the above relation cannot be applied, not even to cases in which the model is reversible and the trajectories are dense on the allowed phase space: the chaotic hypothesis says that the fact that the system is not mathematically an Anosov system is not relevant for physical observations, in most cases. This is similar to the statement that in equilibrium systems the lack of ergodicity of motions is irrelevant in most cases and averages can be computed by assuming ergodicity (*i.e.* by using the microcanonical distribution).

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

(●) When the forcing of the system is let to 0 the above relation degenerates: not only $\langle \sigma \rangle \rightarrow 0$ but also p itself becomes ill defined as its definition involves division by $\langle \sigma \rangle$. Nevertheless by extracting the leading behavior of both sides the fluctuation relation leads to relations between average values of derivatives of dynamical quantities with respect to the intensity of the forcing, *evaluated at zero forcing*, and such relations can be interpreted as Onsager reciprocity relations and Green–Kubo expressions for suitably defined transport coefficients, [Ga02].

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

(●) And one can go beyond various assumptions via the use of equivalence conjectures between different thermostats: for instance Drude’s thermostat model which strictly speaking is not reversible is conjectured to be equivalent to a Gaussian thermostat which is reversible. The Navier–Stokes equation for incompressible fluids, clearly irreversible, is conjectured to be equivalent to a similar reversible equation, [Ga02], as the quoted experiment, [SJ93], shows and as other successive experiments seem to confirm, [GRS02]. The research along the just mentioned lines seems to go quite far and to lead not only to new perspectives but also to new results or confirmations (*i.e.* non contradictions) of the general views in Sections 1,2. Doubts about the whole approach can be legitimately raised, and have been raised, on the grounds that the results are too few and too meager to be really interesting: for instance one can hold against their consideration that they are not even sufficient to give some hint at a derivation of “elementary” relations like Fourier’s law or Ohm’s law. One can only say that time is not

yet ripe to see whether the new methods and ideas lead really anywhere or at least to a better understanding of some of the problems that also the old ones have not been able to tackle, so far, (like the heat conduction laws or the electric conduction laws) in spite of intense research efforts.

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390 (A): Nonequilibrium thermodynamics ? twentyseven comments

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Author index			
A		Maxwell	3
Adler	133, 144	Minlos	155
Aristarchos	50	Monroy	372
Arnold	307	Morrey	242
Asano	273	Moser	307
B		N	
Bohl	47, 50	Newcomb	278, 288
Boltzmann	1, 2	O	
Bowen	126, 132, 197	Onsager	272
Breiman	87	Ornstein	102, 372
Bryuno	288, 295, 297, 323	P	
C		Pöschel	297
Cardano	281	Peierls	272
Chirikov	323	Penrose	227, 242
Choquet	61	Poincaré	50, 278, 288
D		R	
Davie	332	Rüssmann	308
Dobrushin	147, 155	Renij	176
Dyson	263	Ruelle	61, 126, 133, 147, 155, 169, 175, 196, 197, 208, 212, 225, 227, 242, 263, 272
E		Russo	372
Ehrenfest	2, 3	S	
Eliasson	278, 292, 307	Shannon	77
F		Siegel	295, 297, 307, 323
Fisher	155	Sinai	97, 102, 112, 132, 155, 159, 186, 197, 203, 209, 372
G		Smale	144
Garsia	39	Smorodinski	372
Gibbs	3	T	
Ginibre	265, 273	Tartaglia	281
Greene	323	U	
Griffiths	155, 208, 265, 273	Ulam	176
Groeneveld	227, 242	V	
H		Van der Waerden	272
Hepp	292	Van Hove	169, 272
Hypparchos	50	Von Neumann	176
J		W	
Jacobi	32	Weiss	133, 144
K		Weyl	50
Keane	372	Y	
Kolmogorov	307	Yang	263, 273
Krylov	3	Yoccoz	323
L		Yorke	176
Lagrange	47, 50		
Landau	272		
Lanford	147, 155		
Lasota	176		
Lee	263, 273		
Lifchitz	272		
Lindstedt	278, 288		
Livsic	209		
M			
Manning	196		

Subject index	
a	
absolute continuity	8
activity	227
activity, of a polymer	216, 233
algebra, at infinity	158
algebra, of Borel sets	10
algebra, of sets	10
algebra, σ	10
analytically integrable	27
analyticity, at high temperature	240
analyticity, of Gibbs distributions	243
approximability, in distribution and entropy	93
approximation, best	43
automorphism, of the torus	11
average entropy	181
average entropy, upper-semicontinuity	90
average, future	49
average, in quasi periodic motion	29
average, past	49
axiom, of choice	3
axiom, of Zermelo	50
b	
block spins	244
boundary condition	179
boundary condition, open	154
boundary term	179
bound, Siegel-Bryuno	304
bound, Siegel Bryuno b. extension	297
branch, entering	294
branch, exiting	294
branch, null	327
branch, of a self-energy subgraph	295
branch, of tree	283
branch, top b. of a tree	284
bulk energy	149
c	
cancellations, in self-energy graphs	292, 308
cancellations, in standard map	329, 330
circle, deferent	46
circle, epicycle	46
cluster expansion	216
cluster expansion, any activity, no hard cores	230
cluster expansion, oriented hard cores	251
cluster expansion, polymers	219
cluster expansion, small activity	227
cluster expansion, small activity, no hard cores	228
cluster, of lines	293
cluster, of nodes	293
cluster, renormalized self-energy	312
cluster, self-energy	294, 313
code	372
code, multiplicity	105
code, of Lebesgue measure by expansive map	171
code, symbolic	20, 171, 196
code, symbolic for volume measure	136
coding, by interval map	141
coefficients, of Mayer	220
coefficients, of Mayer's expansion	225
compatibility matrix	146, 203
complete analyticity	261
complexity and pressure	185
complexity, of a sequence	71
complexity, with weight	71, 185
conditional probability	146
condition, Bryuno	323
condition, Diophantine	277
condition, strong Diophantine	305
conjugate	12
conjugation potential	349
constant of Boltzmann	234
constant of motion	4
continuity, of entropy	95
continuity, of Gibbs states w.r.t. potential	151, 153
continuity, uniform Hölder	205
contraction, Jacobian	134
contraction, local coefficient	135
contraction, local exponent or rate	135
convergence, of renormalized series	318
convergence, weak	53
convergents	42
convergents, of continued fraction	41
convexity of pressure	179
convexity, strict c. of the pressure	208
coordinate, action-angle	14
coordinate, analytic	23
coordinate, C^∞	23
coordinate, system	23
core, hard	207
core, multidimensional hard	215
correlation function	243
cylinder, base	20
cylinder, set	20, 106
cylinder, specification	20
d	
decimated lattice	244
decimation	168, 240, 241, 249
decimation, finite range	167, 240
decimation, of Markov process	167
decomposition, ergodic	61, 184
decomposition, into pure phases	184
decoration, of a tree branch	285
deferent, circle	46
denominator, small	279
denominator, small d. problem	288
dispersion, vanishing condition	209
dispersion, vanishing condition in L_2	209
distribution, absolutely continuous	132
distribution, Boltzmann-Gibbs	150
distribution, Gibbs	146, 147, 154, 215

distribution, Gibbsian and pressure graph	179	entropy, of a sequence	71
distribution, Gibbsian on \mathbb{Z}^+	160	entropy, of quasi periodic motion	71
distribution, Gibbs on d -dimension lattices	153	entropy, topological	196
distribution, infinite-semiinfinite absolute continuity	163	epicycle	46
distribution, invariant	8	epicycle, circle	46
distribution, Liouville	74	epicycle, mean motion	46
distribution, of a sequence	52, 71	epicycles, no exceptions	47
distribution, of Bernoulli	48	equation, Hamilton Jacobi	279
distribution, on sequences and ergodic	52	equation, of Lorenz	7, 8, 11
distribution, on sequences and mixing	52	equations, DLR	147
distribution, on sequences and non stationary	52	equilibrium point	5
distribution, semiinfinite Gibbsian	160	equivalence of potentials	154
distributions, Gibbs d. regularity	214	equivalence, spin-particle	240
distributions, Gibbsian as eigenvalue problems	163	equivalent potentials	204
distribution, SRB	197, 249	ergode	1, 5
distribution, SRB d. and Fubini's theorem	203	ergodic decomposition	61
distribution SRB, definition	187	ergodic distribution	52
distribution, stationary	6, 51	ergodic, etymology	1
distribution, uniqueness of Gibbs d.	155	ergodic, hypothesis	2
divergence of a vector field	4	ergodicity, of Gibbs states	158
divergences, overlap	292	ergodic motions	55
divisor, small	279	ergodic points	55
divisor, small d. absence	282	ergodic, typically e.	67
divisor, small d. problem	288	ergomonode	2
dynamical system, abstract	8	estimate, of Bryuno	289
dynamical system, conjugation	9	exactly soluble potential	186
dynamical system, continuous	9	exceptional point	51
dynamical system, discrete	8	exceptional symbolic motion	51
dynamical system, isomorphism	9	existence of Gibbs states	150
dynamical system, K	159	expansion, binary	85
dynamical system, metric	8	expansion coefficient	355
dynamical system, of Kepler	16	expansion, decimal	85
dynamical system, topological	8	expansion, Jacobian	134
dynamical system, topologically mixing	111	expansion, local coefficient	135
dynamical system, topologically transitive	111	expansion, local exponent or rate	135
dynamical system, with trivial past or K-d.s.	159	expansion, Mayer's	225, 227
dynamic, symbolic	19	expansion, of SRB in periodic orbits	191
e		exponential	217
energy function	147	exponential mixing	243
energy, in Λ	150	extended nearest neighbor potential	243
energy, in Λ with boundary condition	150	f	
energy per site	160	factor, of dynamical system	99
energy, potential e. per site	147	filling time	45
ensemble, statistical	5	finite intersection property	18
entropy	181	finitely determined system	373
entropy, affinity	88, 92	first integral	4
entropy, average	87, 91, 371	flow, abstract	9
entropy, complete invariant for Bernoulli shifts	372	flow, geodesic	12
entropy, Kolmogorov-Sinai invariant	92	flow, Hamiltonian	5
		flow, metric	9
		flow, on a manifold	5
		flow, quasi-periodic	6
		flow, rotation	6
		flows, ergodicity	38
		flow, topological	9
		formula, Cayley's	225
		formula, of Bohl	47
		formula, Pesin	201
		fraction, continued	41

frequency, of a string	22	kicked rotator	331
frequency, of visit	17, 22	kicked rotator, and KAM	331
function, bimeasurable	11	l	
function, Bryuno f.	323	label, mode l.	285
function, cylindrical	135, 136	label, mode l. of a tree node	286
function, generating canonical map	17	label, momentum l. of a tree branch	286
function, measurable	10	label, number l. of a tree branch	285
function, μ -measurable	10	lattice of cat maps	365
function, nonmeasurable	3	lattice of circle maps	369
function, Riemann integrable	29	lattice of interval maps	369
function, zeta f. of a map	197	lattice of maps	362
g		lemma, of Siegel Bryuno	295
gap, in Perron Frobenius spectrum	59	length, Lebesgue l. of a covering	119
generating function of Gibbs states	179	limit, thermodynamic	177
generator theorem	93	logarithm	217
golden mean	44, 344	m	
graph, count	290	manifold, continuity of stable	128
graph, height of a self-energy g.	299	manifold, density of stable and unstable m.	132
graph, null g.	327	manifold, Hölder continuity of hyperbolic	128
graph, renormalized	312	manifolds	128
graph, self-energy	292	manifold, stable existence	128
graph, self-energy	294	manifold, uniqueness of stable m.	130
graph, self-energy	295	manifold, uniqueness of unstable m.	130
graphs, of compatibility	109	manifold, unstable existence	128
growth, of trees	290	map, abstract hyperbolic	126
h		map, Anosov and connected manifold	131
hard core	240, 369	map, Anosov mixing	130
height of a self-energy graph	299	map, Arnold cat	7
height of a tree	299	map, baker	48, 85
hierarchical model	267, 273	map, bimeasurable	11
history of motion	27	map, Borel	58
history on a partition	17	map, canonical	14, 17
history, portion	22	map, cat and mixing	49
hole-particle symmetry	239	map, cat square root	142
homologue strings	22	map, coding	141
i		map, embedded in a flow	11
inequality, of Chebishev	73	map, expanding on the interval	11
inequality, second Griffiths	265	map, expansive	19, 20
integrability	16, 27	map, hyperbolic 3-dimensional	143, 282
integrability, analytical	16	map, logistic	12
integrability, by quadrature	16	map, Markovian m. of the interval	141, 175
integration, Fubini's formula for conditional i.	151	map, measurable	10
interpolation, Bryuno's i.	325	map, mixing interval m.	170
interpolation string	189	map, non transitive	130
invertibility versus reversibility	198	map, of the interval	8
irrational, quadratic	44	map, of the torus	11
isochronous systems	282	map, rotation	6
isochrony	282	map, standard	323, 325
isochrony of harmonic oscillations	16	map, symplectic	14, 17
isomorphisms, between Gibbs states	371	map, tent	25
isomorphism	12, 371	map, translation	21
isomorphism, code	372	map, Ulam-von Neumann	12, 175
isomorphism, mod(0)	10, 86	matrix, compatibility	104
isomorphism, topological	9	matrix, compatibility	104
isomorphism, weak	372	matrix, compatibility	145
k		matrix, compatibility classes	110
		matrix, mixing	60, 104, 107, 110

matrix, mixing compatibility	110	nonwandering point	132
matrix, multidimensional compatibility	215	number, Bryuno	332
matrix, transfer	241	number, of clusters of scale n	299
matrix, transitive	104, 111	number, of rooted trees	224
matrix, transitive compatibility	110	number, of spanning trees	224
mean rotation	48	number, spiral	143, 281
mean, spiral	143, 281	o	
measurability at infinity	158	orbit, density of periodic o.	131
measure, absolute continuity	8	orbit, periodic o. expansion for SRB	191
measure, absolutely continuous for interval	141	oriented hard core	250
maps	141	oscillations, isochrony	16
measure, absolutely continuous w.r.t. volume	8	oscillator, harmonic	13
measure, complete	10, 13	p	
measure, countably additive	10	pair potential	227, 233
measure, equivalence	8	parameter, of scaling	292
measure, example of incomplete	13	particle hole symmetry	239
measure, Gibbs	146	particle potential	207, 208
measure, invariant	8	partition, analytically regular	18
measure, invariant density	12	partition, atom	17
measure, Lebesgue	10	partition, Borel	17
measure, Riemann	10, 23	partition, C^∞ -regular	18
measure, theory	10	partition function	177, 245
measure, topological	104	partition, generating	94, 103
measure, volume	10	partition, history	17
method of cleanings	261	partition, markovian	105
method of shift of conditionings	261	partition, regular	18
metric, adapted	114, 130, 135	partition, separating	20
metric transitivity	2	partition, topological	18
mixing, between SRB and volume distributions	201	pavement	105
mixing distribution	52	pavement, Markovian	105
mixing Gibbs states	158	pavement, Markovian in two-dimensional	143
mixing, of compatibility matrix	125	maps	143
mixing, of non invariant distributions	201	pavement, Markovian simple construction	143
mixing rate	168	perturbation, analytic	304
mixing time of a matrix	146, 147	phases	184
mixing, topological	112, 186	phase transition	186, 263
model, hierarchical	271	phase transitions absence	256
model, Thirring m.	278	phase transitions, Fisher potential	186
monode	1, 5	phase transitions, Fisher potentials	186
motion, ergodic	54	point, density of periodic p.	131
motion, harmonic	13	point, ergodic	54
motion, integrable by quadrature	27	point, errant	111
motion, mean	46	point, non wandering	111, 132
motion, quasi periodic	15, 277	point, non wandering p. and density of	132
motion, real	57	periodic p.	175
motions, exceptional	51	point, of Ruelle	216
motions, w. defined frequencies	51	polymer	219
motion, symbolic	19, 57, 103	polymer, cluster expansion	218
motion, typically ergodic	67	polymer, compatibility	218
n		polymer, configuration	216, 218
nearest neighbor interaction	346	polymer, expansion smoothness	223
node factor	287	potential, correspondence with Gibbs	208
node, of tree	283	states	204
noninvertible dynamical system	7	potential, decay	256
nonstationary distribution	52	potential, diameter decay	154, 204
non translation invariant potential	226	potential, equivalence	186
		potential, exactly soluble	150, 233
		potential, finite range	

potential, Fisher	159, 168, 185, 186, 242	reversible, system	198
potential, for smooth function	154	root branch	283
potential, for spin systems on \mathbb{Z}^d	214, 215	root, of tree	283
potential, for symbolic dynamics	146	rotation number	18, 48
potential, many body	147	rotation, resonant	30
potential: N-body	233	rotation vector	6, 276
potential, particle	154	rotator	275
potential, particle p. existence	154	rules of Feynman	287
potential, pressure of	177		
potential, renormalized	244	s	
potential, short range	233	scale, of a line	292
potential, with vacuum	207	scale, of a propagator	292
pressure	177, 179	scale, self-energy	295
pressure, of a function	191	scheme, Bernoulli	372
pressure, of Ising potential	185	seed, of divergence	294
principle, variational	184	separating partition	19
probability, conditional	133	sequence, distribution	52
probability distribution	5	sequence, ergodic	35
probability distribution, topological	104	sequence, T -compatible	105
problem, Siegel's	332	sequence, with defined frequencies	22
process, Markov	60, 153, 167	series, Lindstedt	279, 304, 324
process, of Bernoulli	48	series, Lindstedt s.	287
process, stochastic	52	series, renormalized Lindstedt	310
propagator	287	set, analytically regular	23, 24
propagator, dressed	313	set, Borel	10, 13
propagator, scale	292	set, C^∞ -regular	24
propagator, symmetry	311	set, cylinder	20, 106
property, covariance	114	set, non Riemann measurable	25
property, Diophantine	43, 320, 325	shadowing	127
property, hyperbolicity	114	shape, topological s. of a tree	329
property, splitting and hyperbolicity	114, 131	shift, Bernoulli	48, 58, 153
		shift map	160
q		shift, of sequences	104
quadrature	27	short range potential	243
quasi-periodic flow	6	sigma algebra	10
		spatio-temporal chaos	369
r		specification	20
range, of potential	150	spin, configurations	214
rate, of mixing	168	spin, $\frac{n}{2}$	214
rational independence	28	spin, on a lattice	214
rationally independent 3-vectors	281	spin potential	240
rectangle, hyperbolic r.	116	splitting, hyperbolic	115
rectangle, S -r.	116	stability, Hamiltonian	277
regularity of pressure and non uniqueness	186	stable manifold	362
regularity, of SRB distribution	367	stack, Rohlin's	99
renormalization group	271, 273	stack, theorem	100
renormalization, hierarchical model	271	state, Gibbs	146
renormalization, of Lindstedt series	314	stationary distribution	1
renormalization theory	292	statistics, future	198
renormalization, trivial fixed point	272	statistics, of motion	56
renormalized graph value	313	statistics, past	198
renormalized potential	244	statistics, SRB	197
renormalized tree value	313	string, frequency	23
resonance	277, 281	string, interpolating	189
resonance, in standard map	325	string, of symbols	22
resummation, of Lindstedt series	314	structural stability	339, 345
resummation, of self energy graphs	310	subshift, of finite type	104, 109, 196
reversibility	198	subshift, spectral decomposition	110
		surface correction	179
		surface energy	149, 150

surface, locally analytic	23	tori, twistless	278
surface, term	150	torus, resonant	322
symbolic code	20	transfer matrix	241, 249, 252
symbolic dynamics	20	transfer operator	164
symbols, classes	109	transfer operator, algebraic	168
symbol, shadow	127	transfer operator, spectral theory	166
symbols, inessential	109	transitive vacuum	206, 226
symmetric difference	86	transitivity, of compatibility matrix	125
symmetry, particle-hole	239	transitivity, topological	112, 186
system, abstract hyperbolic	126	tree	283
system, ergodic	37	tree, branch	283
system, factor	99	tree, distance	216
system, integrable	16	tree, expansion	285
system, K	159	tree, growth	290
system, mixing	37	tree, height	299
system, Smale	126	tree, length	223, 365
t		tree, length of a set	216
tangent to pressure graph	179	tree, node	283
theorem, Anosov	115, 130	tree, property [P] of	288
theorem, Averintzev–Spitzer	154	tree, representation	283
theorem, Baire	106	tree, value of	285
theorem, Birkhoff	34, 38, 39, 197	u	
theorem, Borel Cantelli	307	unique ergodicity	68
theorem, Breiman	87	uniqueness, of Gibbs distribution	155
theorem, Doob	82, 84, 138, 165	unstable manifold	362
theorem, Fubini on Anosov maps	140	v	
theorem, Fubini t. and SRB	203	vacuum	206, 226
theorem, Hadamard Perron	128	vacuum, particle potential	207
theorem, KAM	277	value, renormalized tree v.	313
theorem, Kouchnirenko	74, 77, 202	variational principle	184
theorem, Kuratowsky	57, 106	variational principle for smooth functions	191
theorem, Lasota Yorke	171	vector, cotangent	12
theorem, Liouville	11	vector, Diophantine	277, 282
theorem, of Rohlin’s stack	100	vector, Diophantine 3–v.	281, 282
theorem, of Sinai on positivity of entropy	159	vector, Pisot–Vijayaraghavan Diophantine	282
theorem, of the generator	96	vector, strongly Diophantine	293
theorem, Ornstein	372	vectors, with Diophantine property	282
theorem, Perron Frobenius	59, 196, 241	w	
theorem, Perron Frobenius t. for compatibility matrices	111	wandering point	132
theorem, Perron Frobenius t. for transitive matrices	111	weakly Markovian chains	243
theorem, Perron Frobenius t. on mixing matrices	60	well defined frequency	27
theorem, quasi-periodic Shannon–McMillan	87	z	
theorem, Radon–Nykodim	82	zeta function	197
theorem, Shannon–McMillan	77, 185		
theorem, Sinai	95, 373		
theorem, Smale’s spectral	112		
theorem, Vitali–Lebesgue	82		
thermodynamic limit	177		
time, mixing	104		
time, mixing	146		
time reversal	198		
topology, weak	53		
tori, invariant	277		
tori, invariant hyperbolic	320		

Citations index			
[AA68]	4, 13, 32, 47, 49, 50, 77, 133, 307	[EE59]	2, 3
[AA69]	102	[EG73]	374
[Ar63]	307	[El96]	278, 295, 297, 307
[AS67]	128, 133	[EM90]	382, 385
[As70]	263	[Fe78]	176
[Av76]	13, 133	[Fe79]	176
[AW68]	112, 133, 144	[Fi67]	243
[BCGNOPS78]	261	[FKGC71]	273
[Be64]	384	[Ga00]3, 213, 221, 223, 238, 273, 379, 380,	384, 386
[BFG03]	252, 340, 366, 371	[Ga01]	287, 307
[BG01]	325, 332, 337	[Ga02]	379, 381, 386, 388
[BGGM98]	307	[Ga72]	273
[BGN80]	261	[Ga72a]	225
[BGW98]	45	[Ga73]	375
[Bi31]	39, 50	[Ga77]	243
[Bi35]	25	[Ga80]	261
[BK94]	366	[Ga82]	17, 25, 307
[BK95]	365, 367, 369, 370, 371	[Ga85]	271
[BK96]	366, 367, 371	[Ga94]	307
[BK97]	366, 367, 371	[Ga94a]	278
[BM94]	332, 337	[Ga94b]	326
[Bo02]	3	[Ga99]	271, 371
[Bo03]	3	[GC95]	380, 388
[Bo09]	1, 3	[GG02]	295, 320, 321
[Bo70]	132, 197	[GG95]	303
[Bo75]	127, 133, 176	[GGM78]	225
[Bo96]	1	[Gi60]	3
[Br57]	87	[Gi70]	265, 273
[Br99]	3	[GJS73]	225
[BS88]	366, 371	[GK69]	225, 239
[Ca76]	112	[GK70]	216
[Ca82]	242	[GK78]	225, 242
[CE80a]	144, 176	[GL03]	380
[Ce99]	3	[GL70]	167
[CEL80]	176	[GLM02]	225
[CF02]	282	[GM68]	236, 237, 239
[CF94]	308	[GM70]	167
[CF96]	308	[GM95]	396
[Ch79]	323	[GM96]	307, 308
[Ch99]	50	[GMK00]	261
[CM01]	50	[GMM73]	223, 225
[CO81]	168, 249, 255, 356	[GMM78]	225
[CO82]	371	[GMR68]	234, 236, 239, 240, 396
[Cv84]	399	[Gr62]	242
[Da94]	332, 337	[GR71]	208, 212
[DGM84]	387	[Gr79]	323
[DIS73]	239	[Gr81]	261
[DJS73]	225	[GR97]	357
[Do68a]	155	[GRS02]	388
[Do68b]	155, 234, 236	[He61]	292
[Do68c]	155	[Ho74]	273
[Do69]	155, 240	[Is76]	242
[DS58]	54, 62, 63, 82, 84, 86, 87, 106, 182, 186	[Ja59]	87
[DS87]	261	[Ja62]	39, 50
[Dy69]	263, 272	[JM96]	366, 367, 371
[Ec75]	225	[JP99]	365, 366, 370, 371
[ECM93]	387	[KH95]	133
		[Ki57]	87
		[Ki64]	50

[KM79]	375	[Ru78]	126, 169, 197, 212
[Kr79]	3	[Ru95]	197, 379, 381
[KS79]	372	[Ru97]	357
[Ku78]	242	[Ru99]	197, 379, 381, 383
[La78]	176	[SF72]	273
[Le11]	47, 48, 50	[Sh49]	77
[Le73]	375	[Sh73]	375
[Le74]	273	[Si68]	197
[Le93]	381	[Si68a]	112, 132, 144
[Li01]	3	[Si68b]	112, 144
[LL67]	272	[Si69b]	132
[Lo63]	8, 170	[Si72]	112, 144, 196, 197, 203
[LR68]	182, 186	[Si77]	13, 197, 203
[LR69]	155	[Si93]	258, 261
[LY52]	263, 273	[SJ93]	386, 388
[LY73]	171, 176	[Sy79]	242
[Ma65]	3	[Th83]	278
[Ma71]	197	[UV47]	176
[Mi79]	176	[VH50]	169, 272
[Mi95]	225	[VW41]	272
[Mo21]	25	[Wa41]	272
[Mo55]	242	[We79]	93
[Mo63]	307	[Wi70]	271
[Mo78]	307	[Wi83]	271
[MR75]	372, 375	[Yo95]	323, 325, 332
[MS67]	223, 225	[Ze68]	381
[MS76]	225		
[Ol88]	261		
[On44]	272		
[Or74]	102, 372, 373, 375		
[OS73]	225		
[OW74]	375		
[Pa67]	57, 60, 94		
[Pe36]	272		
[Pe63]	242		
[Pi??]	176		
[Pi79]	175, 176		
[Pi80]	175, 176		
[Pi81]	175		
[Po85]	50		
[Po86]	297		
[Po93]	287		
[Pr83]	261		
[PY79]	144, 176		
[Ra99]	50		
[Re57]	176		
[Re78]	380		
[Ru01]	308		
[Ru03]	380		
[Ru63]	242		
[Ru66]	68		
[Ru67]	164, 166, 167, 169, 272		
[Ru68]	133		
[Ru69]	61, 68, 93, 155, 186, 216, 220, 225, 240, 273		
[Ru71]	263, 273		
[Ru72]	186, 273		
[Ru73]	273		
[Ru76]	127, 144, 197		
[Ru77]	144, 175, 176		