

Stationary nonequilibrium statistical mechanics

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1. Nonequilibrium.

Systems in stationary nonequilibrium are mechanical systems subject to nonconservative external forces and to thermostat forces which forbid indefinite increase of the energy and allow reaching statistically stationary states. A system Σ is described by the positions and velocities of its n particles $\mathbf{X}, \dot{\mathbf{X}}$, with the particles positions confined to a finite volume container C_0 .

If $\mathbf{X} = (\mathbf{x}_1, \dots, \mathbf{x}_n)$ are the particles positions in a Cartesian inertial system of coordinates, the equations of motion are determined by their masses $m_i > 0$, $i = 1, \dots, n$, by the *potential energy* of interaction $V(\mathbf{x}_1, \dots, \mathbf{x}_n) \equiv V(\mathbf{X})$, by the external nonconservative forces $\mathbf{F}_i(\mathbf{X}, \Phi)$ and by the *thermostat* forces $-\vartheta_i$ as

$$m_i \ddot{\mathbf{x}}_i = -\partial_{\mathbf{x}_i} V(\mathbf{X}) + \mathbf{F}_i(\mathbf{X}; \Phi) - \vartheta_i, \quad i = 1, \dots, n \quad (1.1)$$

where $\Phi = (\varphi_1, \dots, \varphi_q)$ are strength parameters on which the external forces depend. All forces and potentials will be supposed smooth, *i.e.* analytic, in their variables aside from *possible* impulsive elastic forces describing shocks, and with the property: $\mathbf{F}(\mathbf{X}; \mathbf{0}) = \mathbf{0}$. The impulsive forces are allowed here to model possible shocks with the walls of the container C_0 or between hard core particles.

A kind of thermostats are *reservoirs* which may consist of one or more *infinite* systems which are asymptotically in thermal equilibrium and are separated by boundary surfaces from each other as well as from the system: with the latter they interact through short range conservative forces, see Fig.1.

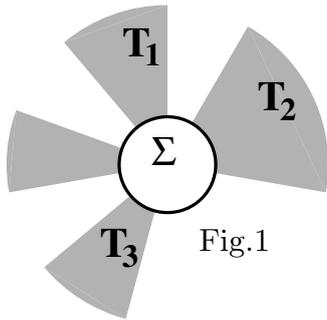


Fig.1

The reservoirs occupy infinite regions of the space outside C_0 , *e.g.* sectors $C_a \subset \mathbb{R}^3$, $a = 1, 2, \dots$, in space and their particles are in a configuration which is typical of an equilibrium state at temperature T_a . This means that the *empirical* probability of configurations in each C_a is Gibbsian with some temperature T_a . In other words the frequency with which a configuration $(\dot{\mathbf{Y}}, \mathbf{Y} + \mathbf{r})$ occurs in a region $\Lambda + \mathbf{r} \subset C_a$ while a configuration $(\dot{\mathbf{W}}, \mathbf{W} + \mathbf{r})$ occurs outside $\Lambda + \mathbf{r}$ (with $\mathbf{Y} \subset \Lambda$, $\mathbf{W} \cap \Lambda = \emptyset$) *averaged*

over the translations $\Lambda + \mathbf{r}$ of Λ by \mathbf{r} (with the restriction that $\Lambda + \mathbf{r} \subset C_a$) is

$$\begin{aligned} \text{average}_{\mathbf{r}+\Lambda \subset C_a} (f_{\Lambda+\mathbf{r}}[(\dot{\mathbf{Y}}, \mathbf{Y} + \mathbf{r}); \dot{\mathbf{W}}, \mathbf{W} + \mathbf{r}]) = \\ = \frac{e^{-\beta_a \left(\frac{1}{2m_a} |\dot{\mathbf{Y}}|^2 + V_a(\mathbf{Y}|\mathbf{W}) \right)}}{\text{normalization}} \end{aligned} \quad (1.2)$$

here m_a is the mass of the particles in the a -th reservoir and $V_a(\mathbf{Y}|\mathbf{W})$ is the energy of the short range potential between pairs of particles in $\mathbf{Y} \subset C_a$ or with one point in \mathbf{Y} and one in \mathbf{W} . Since the configurations in the system and in the thermostats are not random the (1.2) should be considered as an “empirical” probability in the sense that it is the frequency density of the events $\{(\dot{\mathbf{Y}}, \mathbf{Y} + \mathbf{r}); \mathbf{W} + \mathbf{r}\}$: in other words the configurations ω_a in the reservoirs should be “typical” in the sense of probability theory of distributions which are asymptotically Gibbsian.

The property of being “thermostats” means that (1.2) remains true for all times, if initially satisfied.

Mathematically there is a problem at this point: the latter property is either true or false, but a proof of its validity seems out of reach of the present techniques except in very simple cases. Therefore here we follow an intuitive approach and assume that such thermostats exist and, actually, that any configuration which is typical of a stationary state of an infinite size system of interacting particles in the C_a ’s, with physically reasonable microscopic interactions, satisfies the property (1.2).

The above thermostats are examples of “deterministic thermostats” because, together with the system they form a deterministic dynamical system. They are called “Hamiltonian thermostats” and are often considered as the most appropriate models of “physical thermostats”.

A closely related thermostat model is obtained by assuming that the particles outside the system are not in a given configuration but they have a probability distribution whose conditional distributions satisfy (1.2) initially. Also in this case it is necessary to assume that (1.2) remains true for all times, if initially satisfied. Such thermostats are examples of “stochastic thermostats” because their action on the system depends on random variables ω_a which are the *initial* configurations of the particles belonging to the thermostats.

Other kinds of stochastic thermostats are *collision rules* with the container boundary ∂C_0 of Σ : every time a particle collides with ∂C_0 it is reflected with a momentum \mathbf{p} in $d^3\mathbf{p}$ that has a probability distribution proportional to $e^{-\beta_a \frac{1}{2m} \mathbf{p}^2} d^3\mathbf{p}$ where β_a , $a = 1, 2, \dots$ depends on which boundary portion (labeled by $a = 1, 2, \dots$) the collision takes place and $T_a = (k_B \beta_a)^{-1}$ is its “temperature” if k_B is Boltzmann’s constant. Which \mathbf{p} is actually chosen after each collision is determined by a random variable $\omega = (\omega_1, \omega_2, \dots)$.

The distinction between stochastic and deterministic thermostats ultimately rests on what we call “system”. If reservoirs or the randomness generators are included in the system then the system becomes deterministic (possibly infinite); and finite deterministic thermostats can also be regarded as simplified models for infinite reservoirs, see Sect.4 below.

It is also possible, and convenient, to consider “finite deterministic thermostats” in which ϑ is a force *only* depending upon the configuration of the n particles in their finite container C_0 and there are no “external” forces.

Examples of finite deterministic thermostats are forces obtained by imposing a non-holonomic constraint via some *ad hoc* principle like the Gauss' principle. For instance if a system of particles driven by a force $\mathbf{G}_i \stackrel{def}{=} -\partial_{\mathbf{x}_i} V(\mathbf{X}) + \mathbf{F}_i(\mathbf{X})$ is enclosed in a box C_0 and $\boldsymbol{\vartheta}$ is a thermostat enforcing an anholonomic constraint $\psi(\dot{\mathbf{X}}, \mathbf{X}) \equiv 0$ via Gauss' principle then

$$\boldsymbol{\vartheta}_i(\dot{\mathbf{X}}, \mathbf{X}) = \partial_{\dot{\mathbf{x}}_i} \psi(\dot{\mathbf{X}}, \mathbf{X}) \cdot \left[\frac{\sum_j \dot{\mathbf{x}}_j \cdot \partial_{\mathbf{x}_j} \psi(\dot{\mathbf{X}}, \mathbf{X}) + \frac{1}{m} \mathbf{G}_j \cdot \partial_{\dot{\mathbf{x}}_j} \psi(\dot{\mathbf{X}}, \mathbf{X})}{\sum_j \frac{1}{m} (\partial_{\dot{\mathbf{x}}_j} \psi(\dot{\mathbf{X}}, \mathbf{X}))^2} \right] \quad (1.3)$$

Gauss' principle says that the force which needs to be added to the other forces \mathbf{G}_i acting on the system minimizes $\sum_i \frac{(\mathbf{G}_i - m_i \mathbf{a}_i)^2}{m_i}$, given $\dot{\mathbf{X}}, \mathbf{X}$, among all accelerations \mathbf{a}_i which are compatible with the constraint ψ .

It should be kept in mind that the only known examples of mathematically treatable thermostats modeled by infinite reservoirs are cases in which the thermostat particles are either noninteracting particles or linear (*i.e.* noninteracting) oscillators. *For simplicity stochastic or infinite thermostats will not be considered* here and we restrict attention to finite deterministic systems.

In general in order that a force $\boldsymbol{\vartheta}$ can be considered a deterministic “thermostat force” a further property is necessary: namely that the system evolves according to (1.1) towards a *stationary state*. This means that for all initial particles configurations $(\dot{\mathbf{X}}, \mathbf{X})$, *except possibly for a set of zero phase space volume*, any smooth function $f(\dot{\mathbf{X}}, \mathbf{X})$ evolves in time so that, if $S_t(\dot{\mathbf{X}}, \mathbf{X})$ denotes the configuration into which the initial data evolve in time t according to (1.1), then the limit

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T f(S_t(\dot{\mathbf{X}}, \mathbf{X})) dt = \int f(z) \mu(dz) \quad (1.4)$$

exists and is independent of $(\dot{\mathbf{X}}, \mathbf{X})$. The probability distribution μ is then called the *SRB distribution* for the system. The maps S_t will have the group property $S_t \cdot S_{t'} = S_{t+t'}$ and the SRB distribution μ will be invariant under time evolution.

It is important to stress that the requirement that the exceptional configurations form just a set of zero phase volume (rather than a set of zero probability with respect to another distribution, singular with respect to the phase volume) is a strong assumption and *it should be considered an axiom of the theory*: it corresponds to the assumption that the initial configuration is prepared as a typical configuration of an equilibrium state, which by the classical equidistribution axiom of equilibrium statistical mechanics is a typical configuration with respect to the phase volume .

For this reason the SRB distribution is said to describe a stationary nonequilibrium state of the system. It depends on the parameters on which the forces acting on the system depend, *e.g.* $|C_0|$ (volume), $\boldsymbol{\Phi}$ (strength of the forcings), $\{\beta_a^{-1}\}$ (temperatures) *etc.* The collection of SRB distributions obtained by letting the parameters vary defines a *nonequilibrium ensemble*.

In the stochastic case the distribution μ is required to be invariant in the sense that it can be regarded as a marginal distribution of an invariant distribution for the larger (deterministic) system formed by the thermostats and the system itself.

References: [EM90], [Ru97a], [EPR99].

2. Nonequilibrium thermodynamics

The key problem of nonequilibrium statistical mechanics is to derive a macroscopic “nonequilibrium thermodynamics” in a way similar to the derivation of equilibrium thermodynamics from equilibrium statistical mechanics.

The first difficulty is that nonequilibrium thermodynamics is not well understood. For instance there is no (agreed upon) definition of *entropy* of a nonequilibrium stationary state, while it should be kept in mind that the effort to find the microscopic interpretation of equilibrium entropy, as defined by Clausius, was a driving factor in the foundations of equilibrium statistical mechanics.

The importance of entropy in classical equilibrium thermodynamics rests on the implication of universal, parameter free, relations which follow from its existence (*e.g.* $\partial_V \frac{1}{T} \equiv \partial_U \frac{p}{T}$ if U is the internal energy, T the absolute temperature and p the pressure of a simple homogeneous material).

Are there universal relations among averages of observables with respect to SRB distributions?

The question has to be posed for systems “really” out of equilibrium, *i.e.* for $\Phi \neq \mathbf{0}$ (see (1.1)): in fact there is a well developed theory of the derivatives with respect to Φ of averages of observables evaluated at $\Phi = \mathbf{0}$. The latter theory is often called, and here we shall do so as well, *classical nonequilibrium thermodynamics* or *near equilibrium thermodynamics* and it has been quite successfully developed on the basis of the notions of equilibrium thermodynamics, paying particular attention on the macroscopic evolution of systems described by macroscopic continuum equations of motion.

“Stationary nonequilibrium statistical mechanics” will indicate a theory of the relations between averages of observables with respect to SRB distributions. Systems so large that their volume elements can be regarded as being in locally stationary nonequilibrium states could also be considered. This would extend the familiar “local equilibrium states” of classical nonequilibrium thermodynamics: however they are not considered here. This means that we shall not attempt at finding the macroscopic equations regulating the time evolution of continua locally in nonequilibrium stationary states but we shall only try to determine the properties of their “volume elements” assuming that the time scale for the evolution of large assemblies of volume elements is slow compared to the time scales necessary to reach local stationarity.

References: [DGM84], [Le93], [Ru97a], [Ru99a], [Ga98], [GL03], [Ga04].

3. Chaotic hypothesis

In equilibrium statistical mechanics the *ergodic hypothesis* plays an important conceptual role as it implies that the motions of ergodic systems have a SRB statistics and that the latter coincides with the Liouville distribution on the energy surface.

An analogous role has been proposed for the *chaotic hypothesis*: which states that

Motion developing on the attracting set of a chaotic system can be regarded as an Anosov flow.

This means that the attracting sets of chaotic systems, physically defined as systems with at least one positive Lyapunov exponent, can be regarded as smooth surfaces on which motion is highly unstable:

- (i) around every point x a curvilinear coordinate system can be established which has three planes tangent at x , varying continuously with x , which are *covariant* (*i.e.* are coordinate planes at a point x which are mapped, by the evolution S_t , into the corresponding coordinate planes around $S_t x$) and
- (ii) the planes are of three types, *stable, unstable and marginal*, with respective positive dimensions d_s, d_u and 1: infinitesimal lengths on the stable plane and on the unstable plane of any point contract at exponential rate as time proceeds towards the future or towards the past. The length along the marginal direction neither contracts nor expands (*i.e.* it varies around the initial value staying bounded away from 0 and ∞): its tangent vector is parallel to the flow. In cases in which time evolution is discrete, and determined by a map S , the marginal direction is missing.
- (iii) the contraction over a time t , positive for lines on the stable plane and negative for those on the unstable plane, is exponential, *i.e.* lengths are contracted by a factor uniformly bounded by $Ce^{-\kappa|t|}$ with $C, \kappa > 0$.
- (iv) there is a dense trajectory.

It has to be stressed that the chaotic hypothesis concerns physical systems: mathematically *it is very easy to find dynamical systems for which it does not hold*. At least as easy as it is to find systems in which the ergodic hypothesis does not hold (*e.g.* harmonic lattices or black body radiation). However, if suitably interpreted, the ergodic hypothesis leads even for these systems to physically correct results (the specific heats at high temperature, the Raileigh-Jeans distribution at low frequencies). Moreover the failures of the ergodic hypothesis in physically important systems have led to new scientific paradigms (like quantum mechanics from the specific heats at low temperature and Planck's law).

Since physical systems are almost always not Anosov systems it is very likely that probing motions in extreme regimes will make visible the features that distinguish Anosov systems from non Anosov systems: much as it happens with the ergodic hypothesis.

The interest of the hypothesis is to provide a framework in which properties like the existence of an SRB distribution is *a priori* guaranteed together with an expression for it which can be used to work with formal expressions of the averages of the observables: the

role of Anosov systems in chaotic dynamics is similar to the role of harmonic oscillators in the theory of regular motions. They are the paradigm of chaotic systems, as the harmonic oscillators are the paradigm of order. Of course the hypothesis is only a beginning and one has to learn how to extract information from it, as it was the case with the use of the Liouville distribution once the ergodic hypothesis guaranteed that it was the appropriate distribution for the study of the statistics of motions in equilibrium situations.

References: [Ru76], [GC95], [Ru97a], [Ga98], [GBG04].

4. Heat, temperature and entropy production

The amount of *heat* \dot{Q} that a system produces while in a stationary state is naturally identified with the work that the thermostat forces ϑ perform per unit time

$$\dot{Q} = \sum_i \vartheta_i \cdot \dot{\mathbf{x}}_i \quad (4.1)$$

A system may be in contact with several reservoirs: in models this will be reflected by a decomposition

$$\vartheta = \sum_a \vartheta^{(a)}(\dot{\mathbf{X}}, \mathbf{X}) \quad (4.2)$$

where $\vartheta^{(a)}$ is the force due to the a -th thermostat and depends on the coordinates of the particles which are in a region $\Lambda_a \subseteq C_0$ of a decomposition $\cup_{a=1}^m \Lambda_a = C_0$ of the container C_0 occupied by the system ($\Lambda_a \cap \Lambda_{a'} = \emptyset$ if $a \neq a'$).

From several studies based on simulations of finite thermostated systems of particles arose the proposal to consider the average of the phase space contraction $\sigma^{(a)}(\dot{\mathbf{X}}, \mathbf{X})$ due to the a -th thermostat

$$\sigma^{(a)}(\dot{\mathbf{X}}, \mathbf{X}) \stackrel{def}{=} \sum_j \partial_{\dot{\mathbf{x}}_j} \cdot \vartheta_j^{(a)}(\dot{\mathbf{X}}, \mathbf{X}) \quad (4.3)$$

and to identify it with the *rate of entropy creation* in the a -th thermostat.

Another key notion in thermodynamics is the *temperature* of a reservoir; in the infinite deterministic thermostats case, of Sect.1, it is defined as $(k_B \beta_a)^{-1}$ but in the finite deterministic thermostats considered here it needs to be defined. If there are m reservoirs with which the system is in contact one sets

$$\begin{aligned} \sigma_+^{(a)} &\stackrel{def}{=} \langle \sigma^{(a)}(\dot{\mathbf{X}}, \mathbf{X}) \rangle \equiv \int \sigma^{(a)}(\dot{\mathbf{X}}, \mathbf{X}) \mu(d\dot{\mathbf{X}} d\mathbf{X}) \\ \dot{Q}_a &\stackrel{def}{=} \sum_i \vartheta_i^{(a)} \cdot \dot{\mathbf{x}}_i \end{aligned} \quad (4.4)$$

where μ is the SRB distribution describing the stationary state. It is natural to define the *absolute temperature* of the a -th thermostat to be

$$T_a = \frac{\langle \dot{Q}_a \rangle}{k_B \sigma_+^{(a)}}. \quad (4.5)$$

It is not clear that $T_a > 0$: this happens in a rather general class of models and it would be desirable, for the interpretation that is proposed here, that it could be considered a property to be added to the requirements that the forces $\boldsymbol{\vartheta}^{(a)}$ be thermostats models.

An important class of thermostats for which the property $T_a > 0$ holds can be described as follows. Imagine N particles in a container C_0 interacting via a potential $V_0 = \sum_{i < j} \varphi(\mathbf{q}_i - \mathbf{q}_j) + \sum_j V'(\mathbf{q}_j)$ (where V' models external conservative forces like obstacles, walls, gravity, ...) and, furthermore, interacting with M other systems Σ_a , of N_a particles of mass m_a , in containers C_a contiguous to C_0 . The latter will model M parts of the system in contact with thermostats at temperatures T_a , $a = 1, \dots, M$.

The coordinates of the particles in the a -th system Σ_a will be denoted \mathbf{x}_j^a , $j = 1, \dots, N_a$, and they will interact with each other via a potential $V_a = \sum_{i, j} \varphi_a(\mathbf{x}_i^a - \mathbf{x}_j^a)$. Furthermore there will be an interaction between the particles of each thermostat and those of the system via potentials $W_a = \sum_{i=1}^N \sum_{j=1}^{N_a} w_a(\mathbf{q}_i - \mathbf{x}_j^a)$, $a = 1, \dots, M$.

The potentials will be assumed to be either hard core or non singular potentials and the external V' is supposed to be at least such that it forbids existence of obvious constants of motion.

The temperature of each Σ_a will be defined by the total kinetic energy of its particles, *i.e.* by $K_a = \sum_{j=1}^{N_a} \frac{1}{2} m_a (\dot{\mathbf{x}}_j^a)^2 \stackrel{def}{=} \frac{3}{2} N_a k_B T_a$: the particles of the a -th thermostat will be kept at constant temperature by further forces $\boldsymbol{\vartheta}_j^a$. The latter are defined by imposing via a Gaussian constraint that K_a is a constant of motion (see (1.3) with $\psi \equiv K_a$). This means that the equations of motion are

$$\begin{aligned} m \ddot{\mathbf{q}}_j &= -\partial_{\mathbf{q}_j} (V_0(\mathbf{Q}) + \sum_{a=1}^{N_a} W_a(\mathbf{Q}, \mathbf{x}^a)) \\ m_a \ddot{\mathbf{x}}_j^a &= -\partial_{\mathbf{x}_j^a} (V_a(\mathbf{x}^a) + W_a(\mathbf{Q}, \mathbf{x}^a)) - \boldsymbol{\vartheta}_j^a \end{aligned} \quad (4.6)$$

and an application of Gauss' principle yields $\boldsymbol{\vartheta}_j^a = \frac{L_a - \dot{V}_a}{3N_a k_B T_a} \dot{\mathbf{x}}_j^a \stackrel{def}{=} \alpha^a \dot{\mathbf{x}}_j^a$ where L_a is the work per unit time done by the particles in C_0 on the particles of Σ_a and V_a is their potential energy.

In this case the partial divergence $\sigma^a \equiv (3N_a - 1)\alpha^a$ is, up to a constant factor $(1 - \frac{1}{3N_a})$,

$$\sigma_a = \frac{L_a}{k_B T_a} - \frac{\dot{V}_a}{k_B T_a} \quad (4.7)$$

and it will make (4.5) satisfied with $T_a > 0$ because L_a can be naturally interpreted as *heat* Q_a ceded, per unit time, by the particles in C_0 to the subsystem Σ_a (hence to the a -th thermostat because the temperature of Σ_a is constant), while the derivative of V_a *will not contribute to the value of* σ_+^a . The phase space contraction rate is, *neglecting the total*

derivative terms (and $O(N_a^{-1})$,

$$\sigma_{true}(\dot{\mathbf{X}}, \mathbf{X}) = \sum_{a=1}^{N_a} \frac{\dot{Q}_a}{k_B T_a}. \quad (4.8)$$

where the subscript “true” is to remind that an additive total derivative term distinguishes it from the complete phase space contraction.

Remarks: (1) The (4.8) provides the motivation of the name “entropy creation rate” attributed to the phase space contraction σ . Note that in this way the definition of entropy creation is “reduced” to the equilibrium notion because what is being defined is the entropy increase of the thermostats which have to be considered in equilibrium. No attempt is made here to define the entropy of the stationary state. Nor any attempt is made to define the notion of temperature of the nonequilibrium system in C_0 (the T_a are temperatures of the Σ_a , not of the particles in C_0). This is an important point as it leaves open the possibility of envisaging the notion of “local equilibrium” which becomes necessary in the approximation (not considered here) in which the system is regarded as a continuum.

(2) In the above model another viewpoint is possible: *i.e.* to consider the system to consist of only the N particles in C_0 and the M systems Σ_a to be thermostats. From this point of view the it can be considered a model of a system subject to external thermostats generalizing the sense of Sec. 1. The Gibbs distribution characterizing the infinite thermostats of Sect.1 becomes in this case the constraint that the kinetic energies K_a are constants, enforced by the Gaussian forces. In the new viewpoint a more appropriate definition of entropy creation rate should be simply the *r.h.s.* of (4.8), *i.e. the work per unit time done by the forces of the system on the thermostats divided by the temperature of the thermostats.* The (4.8) suggests a different and general definition of entropy creation rate, applicable also to thermostats that are often considered “more physical”: it neglects the often very large exchanges of energy internal to the thermostats. In the example (4.6) the new definition differs from the the phase space contraction rate by a total time derivative, *i.e.* rather trivially for the purposes of the following.

References: [EM90], [GC95], [Ru96], [Ru97b], [Ga04].

5. Thermodynamic fluxes and forces

Nonequilibrium stationary states depend upon external parameters φ_j like the temperatures T_a of the thermostats or the size of the force parameters $\Phi = (\varphi_1, \dots, \varphi_q)$, see (1.1). Nonequilibrium thermodynamics is well developed at “low forcing”: strictly speaking this means that it is widely believed that we understand properties of the derivatives of the averages of observables with respect to the external parameters *if evaluated at* $\varphi_j = 0$. Important notions are the notions of *thermodynamic fluxes* J_i and of *thermodynamic forces* φ_i ; hence it seems important to extend such notions to nonequilibrium systems (*i.e.* $\Phi \neq \mathbf{0}$).

A possible extension could be to define the thermodynamic flux J_i associated with a force φ_i as $J_i = \langle \partial_{\varphi_i} \sigma \rangle_{SRB}$ where $\sigma(\mathbf{X}, \dot{\mathbf{X}}; \Phi)$ is the volume contraction per unit time. This definition seems appropriate in several concrete cases that have been studied and it is appealing for its generality.

An interesting example is provided by the model of thermostated system in (4.6): if the container of the system is a box with periodic boundary conditions one can imagine to add an extra constant force \mathbf{E} acting on the particles in the container. Imagining the particles to be charged by a charge e and regarding such force as an electric field the first equation in (4.6) is modified by the addition of a term $e\mathbf{E}$.

The constraints on the thermostats temperatures imply that σ depends also on \mathbf{E} : in fact, if $\mathbf{J} = e \sum_j \dot{\mathbf{q}}_j$ is the electric current, energy balance implies $\dot{U}_{tot} = \mathbf{E} \cdot \mathbf{J} - \sum_a (L_a - \dot{V}_a)$ if U_{tot} is the sum of *all* kinetic and potential energies. Then the phase space contraction $\sum_a \frac{L_a - \dot{V}_a}{T_a}$ can be written, to first order in the temperature variations δT_a with respect to a common value $T_a = T$, as $-\sum_a \frac{L_a - \dot{V}_a}{T} \frac{\delta T_a}{T} + \frac{\mathbf{E} \cdot \mathbf{J} - \dot{U}_{tot}}{T}$ hence σ_{true} , see (4.8), is

$$\sigma_{true} = \frac{\mathbf{E} \cdot \mathbf{J}}{k_B T} - \sum_a \frac{\dot{Q}_a}{k_B T} \frac{\delta T_a}{T} \quad (5.1)$$

The definition and extension of the conjugacy between thermodynamic forces and fluxes is compatible with the key results of classical nonequilibrium thermodynamics, at least as far as Onsager reciprocity and Green-Kubo's formulae are concerned. It can be checked that if the equilibrium system is *reversible*, *i.e.* if there is an isometry I on phase space which anticommutes with the evolution ($IS_t = S_{-t}I$ in the case of continuous time dynamics $t \rightarrow S_t$ or $IS = S^{-1}I$ in the case of discrete time dynamics S) then, shortening $(\dot{\mathbf{X}}, \mathbf{X})$ into x , and defining $L_{ij} \stackrel{def}{=} \partial_{\Phi_i} J_j|_{\Phi=0} \equiv \partial_{\Phi_i} \langle \partial_{\Phi_j} \sigma(x; \Phi) \rangle_{SRB}|_{\Phi=0}$

$$\begin{aligned} L_{ij} &= \partial_{\Phi_j} J_i|_{\Phi=0} = \\ &= \frac{1}{2} \int_{-\infty}^{\infty} \langle \partial_{\Phi_j} \sigma(S_t x; \Phi) \partial_{\Phi_i} \sigma(x; \Phi) \rangle_{SRB} \Big|_{\Phi=0} dt = L_{ji} \end{aligned} \quad (5.2)$$

The $\sigma(x; \Phi)$ plays the role of ‘‘Lagrangian’’ generating the duality between forces and fluxes. The extension of the duality just considered might be of interest in situations in which $\Phi \neq \mathbf{0}$.

References: [DGM84],[Ga96],[GR97].

6. Fluctuations

As in equilibrium, large statistical fluctuations of observables are of great interest and already there is, at the moment, a rather large set of experiments dedicated to the analysis of large fluctuations in stationary states out of equilibrium.

If one defines the dimensionless phase space contraction

$$p(x) = \frac{1}{\tau} \int_0^\tau \frac{\sigma(S_t x)}{\sigma_+} dt \quad (6.1)$$

(see also (4.8)) then there exists $p^* \geq 1$ such that the probability P_τ of the event $p \in [a, b]$ with $[a, b] \subset (-p^*, p^*)$ has the form

$$P_\tau(p \in [a, b]) = \text{const} e^{\tau \max_{p \in [a, b]} \zeta(p) + O(1)} \quad (6.2)$$

with $\zeta(p)$ analytic in $(-p^*, p^*)$. The function $\zeta(p)$ can be conveniently normalized to have value 0 at $p = 1$ (*i.e.* at the average value of p).

Then, *in Anosov systems which are reversible and dissipative* (see Sect.5) a general symmetry property, called the *fluctuation theorem* and reflecting the reversibility symmetry, yields the *parameterless* relation

$$\zeta(-p) = \zeta(p) - p\sigma_+ \quad p \in (-p^*, p^*) \quad (6.3)$$

This relation is interesting because it has no free parameters, in other words it is *universal* for reversible dissipative Anosov systems. In connection with the duality fluxes-forces in Sec.5, it can be checked to reduce to the Green–Kubo formula and to Onsager reciprocity, see (5.2), in the case in which the evolution depends on several fields Φ and $\Phi \rightarrow \mathbf{0}$ (of course the relation becomes trivial as $\Phi \rightarrow \mathbf{0}$ because $\sigma_+ \rightarrow 0$ and to obtain the result one has first to divide both sides by suitable powers of the fields Φ).

A more informal (but imprecise) way of writing (6.2),(6.3) is

$$\frac{P_\tau(p)}{P_\tau(-p)} = e^{\tau p \sigma_+ + O(1)}, \quad \text{for all } p \in (-p^*, p^*) \quad (6.4)$$

where $P_\tau(p)$ is the probability density of p . An obvious but interesting consequence of (6.4) is that

$$\langle e^{-\tau p \sigma_+} \rangle_{SRB} = 1 \quad (6.5)$$

in the sense that $\frac{1}{\tau} \log \langle e^{-\tau p \sigma_+} \rangle_{SRB} \xrightarrow{\tau \rightarrow \infty} 0$.

Occasionally systems with singularities have to be considered: in such cases the relation (6.3) may change in the sense that the function $\zeta(p)$ may be not analytic. In such cases one expects that the relation holds in the largest analyticity interval symmetric around the origin. In Anosov systems and also in various cases considered in the literature such interval contains the interval $(-1, 1)$.

Note that in the theory of fluctuations of the time averages p we can replace σ by any other *bounded* quantity which is a total time derivative: hence, in the example discussed above, it can be replaced by σ_{true} , see (5.1), which has a natural physical meaning.

It is important to remark that the above fluctuation relation is the first representative of several consequences of the reversibility and chaotic hypotheses. For instance given F_1, \dots, F_n *arbitrary* observables which are (say) odd under time reversal I (*i.e.* $F(Ix) = -F(x)$) and given n functions $t \in [-\frac{\tau}{2}, \frac{\tau}{2}] \rightarrow \varphi_j(t)$, $j = 1, \dots, n$ one can ask which is the probability that $F_j(S_t x)$ “closely follows” the *pattern* $\varphi_j(t)$ and at the same time

$\frac{1}{\tau} \int_0^\tau \frac{\sigma(S_\theta x)}{\sigma_+} d\theta$ has value p . Then calling $P_\tau(F_1 \sim \varphi_1, \dots, F_n \sim \varphi_n, p)$ the probability of this event, which we write in the imprecise form corresponding to (6.4) for simplicity, and defining $I\varphi_j(t) \stackrel{def}{=} -\varphi_j(-t)$ it is

$$\frac{P_\tau(F_1 \sim \varphi_1, \dots, F_n \sim \varphi_n, p)}{P_\tau(F_1 \sim I\varphi_1, \dots, F_n \sim I\varphi_n, -p)} = e^{\tau\sigma_+ p}, \quad (6.6)$$

for $p \in (-p^*, p^*)$, which is remarkable because it is parameterless and at the same time surprisingly independent of the choice of the observables F_j . The relation (6.6) has far reaching consequences: for instance if $n = 1$ and $F_1 = \partial_{\Phi_i} \sigma(x; \Phi)$ the relation (6.6) has been used to derive the mentioned Onsager reciprocity and Green–Kubo’s formulae at $\Phi = \mathbf{0}$.

Eq. (6.6) can be read as follows: the probability that the observables F_j follow given evolution patterns φ_j conditioned to entropy creation rate $p\sigma_+$ is *the same* that they follow the time reversed patterns if conditioned to entropy creation rate $-p\sigma_+$. In other words to change the sign of time it is *just* sufficient to reverse the sign of entropy creation rate, no “extra effort” is needed.

References: [Si72],[Si94],[ECM93],[GC85],[Ga96],[GR97],[Ga99],[GBG04],[BGGZ05].

7. Fractal attractors. Pairing. Time reversal.

Attracting sets (*i.e.* sets which are the closure of attractors) are fractal in most dissipative systems. However the chaotic hypothesis assumes that fractality can be neglected. Aside from the very interesting cases of systems close to equilibrium, in which the closure of an attractor is the whole phase space (under the chaotic hypothesis, *i.e.* if the system is Anosov) hence is not fractal serious problems arise in preserving validity of the fluctuation theorem.

The reason is very simple: if the attractor closure is smaller than phase space then it is to be expected that time reversal will change the attractor into a repeller disjoint from it. Thus even if the chaotic hypothesis is assumed, so that the attracting set \mathcal{A} can be considered a smooth surface, the motion on the attractor will not be time reversal symmetric (as its time reversal image will develop on the repeller). One can say that an attracting set with dimension lower than that of phase space in a time reversible system corresponds to a *spontaneous breakdown of time reversal symmetry*.

It has been noted however that there are classes of systems, forming a large set in the space of evolutions depending on a parameter Φ , in which geometric reasons imply that if beyond a critical value Φ_c the attracting set becomes smaller than phase space then a map I_P is generated mapping the attractor \mathcal{A} into the repeller \mathcal{R} , and *viceversa*, such that I_P^2 is the identity on $\mathcal{A} \cup \mathcal{R}$ and I_P commutes with the evolution: therefore the composition $I \cdot I_P$ is a time reversal symmetry (*i.e.* it anticommutes with evolution) for the motions on the attracting set \mathcal{A} (as well as on the repeller \mathcal{R}).

In other words the time reversal symmetry in such systems “cannot be broken”: if spontaneous breakdown occurs (*i.e.* \mathcal{A} is not mapped into itself under time reversal I) a new symmetry I_P is spawned and $I \cdot I_P$ is a new time reversal symmetry (an analogy with the spontaneous violation of time reversal in quantum theory, where time reversal T is violated but TCP is still a symmetry: so T plays the role of I and CP that of I_P).

Thus a fluctuation relation will hold for the phase space contraction of the motions taking place on the attracting set for the class of systems with the geometric property mentioned above (technically the latter is called *axiom C* property).

This is interesting but it still is quite far from being checkable even in numerical experiments. There are nevertheless systems in which also a *pairing property* holds: this means that, considering the case of discrete time maps S , the Jacobian matrix $\partial_x S(x)$ has $2N$ eigenvalues that can be labeled, in decreasing order, $\lambda_N(x), \dots, \lambda_{\frac{1}{2}N}(x), \dots, \lambda_1(x)$ with the remarkable property that $\frac{1}{2}(\lambda_{N-j}(x) + \lambda_j(x)) \stackrel{def}{=} \alpha(x)$ is j -independent. In such systems a relation can be established between phase space contractions in the full phase space and on the surface of the attracting set: the fluctuation theorem for the motion on the attracting set can therefore be related to the properties of the fluctuations of the total phase space contraction measured on the attracting set (which includes the contraction transversal to the attracting set) and if $2M$ is the attracting set dimension and $2N$ is the total dimension of phase space it is, in the analyticity interval $(-p^*, p^*)$ of the function $\zeta(p)$,

$$\zeta(-p) = \zeta(p) - p \frac{M}{N} \sigma_+ \quad (7.1)$$

which is an interesting relation. It is however very difficult to test in mechanical systems because in such systems it seems very difficult to make the field so high to see an attracting set thinner than the whole phase space and *still* observe large fluctuations.

References: [DM96], [Ga99].

8. Nonequilibrium ensembles and their equivalence

Given a chaotic system the collection of the SRB distributions associated with the various control parameters (volume, density, external forces, ...) forms an “ensemble” describing the possible stationary states of the system and their statistical properties.

As in equilibrium one can imagine that the system can be described equivalently in several ways at least when the system is large (“in the thermodynamic” or “macroscopic limit”). In nonequilibrium equivalence can be quite different and more structured than in equilibrium because one can imagine to change not only the control parameters but also the thermostating mechanism.

It is intuitive that a system may behave in the same way under the influence of different thermostats: the important phenomenon being the extraction of heat and not the way in which it is extracted from the system. Therefore one should ask when two systems are “physically equivalent”, *i.e.* when the SRB distributions associated with them give the

same statistical properties for the same observables, at least for the *very few* observables which are macroscopically relevant. The latter may be a few more than the usual ones in equilibrium (temperature, pressure, density, ...) and include currents, conductibilities, viscosities, ... but they will always be very few compared to the (infinite) number of functions on phase space.

As an example consider a system of N interacting particles (say hard spheres) of mass m moving in a periodic box C_0 of side L containing a regular array of spherical scatterers (a basic model for electrons in a crystal) which reflect particles, elastically and are arranged so that no straight line exists in C_0 which avoids the obstacles (to eliminate obvious constants of motion). An external field $E\mathbf{u}$ acts also along the \mathbf{u} -direction: hence the equations of motion are

$$m\ddot{\mathbf{x}}_i = \mathbf{f}_i + E\mathbf{u} - \boldsymbol{\vartheta}_i \quad (8.1)$$

where \mathbf{f}_i are the interparticle and scatterers-particles forces and $\boldsymbol{\vartheta}_i$ are the thermostating forces. The following thermostats models have been considered

- (1) $\boldsymbol{\vartheta}_i = \nu \dot{\mathbf{x}}_i$ (*viscosity thermostat*)
- (2) immediately after elastic collision with an obstacle the velocity is rescaled to a prefixed value $\sqrt{3k_B T m^{-1}}$ for some T (*Drude's thermostat*)
- (3) $\boldsymbol{\vartheta}_i = \frac{\mathbf{E} \cdot \sum_i \dot{\mathbf{x}}_i}{\sum_i \dot{\mathbf{x}}_i^2}$ (*Gauss' thermostat*)

The first two are not reversible. At least not manifestly such, because the natural time reversal, *i.e.* change of velocity sign, is not a symmetry (there might be however more hidden, hitherto unknown, symmetries which anticommute with time evolution). The third is reversible and time reversal is just the change of the velocity sign. The third thermostat model generates a time evolution in which the total kinetic energy K is constant.

Let $\mu'_\nu, \mu''_T, \mu'''_K$ be the SRB distributions for the system in a container C_0 with volume $|C_0| = L^3$ and density $\rho = \frac{N}{L^3}$ fixed. Imagine to tune the values of the control parameters ν, T, K in such a way that $\langle \text{kinetic energy} \rangle_\mu = \mathcal{E}$, *with the same* \mathcal{E} for $\mu = \mu'_\nu, \mu''_T, \mu'''_K$ and consider a *local* observable $F(\dot{\mathbf{X}}, \mathbf{X}) > 0$ depending only on the coordinates of the particles located in a region $\Lambda \subset C_0$. Then a reasonable conjecture is that

$$\lim_{\substack{L \rightarrow \infty \\ \frac{N}{L^3} = \rho}} \frac{\langle F \rangle_{\mu'_\nu}}{\langle F \rangle_{\mu''_T}} = \lim_{\substack{L \rightarrow \infty \\ \frac{N}{L^3} = \rho}} \frac{\langle F \rangle_{\mu'_\nu}}{\langle F \rangle_{\mu'''_K}} = 1 \quad (8.2)$$

if the limits are taken at fixed F (hence at fixed Λ while $L \rightarrow \infty$). The conjecture is an open problem: it illustrates, however, the a kind of questions arising in nonequilibrium statistical mechanics.

References: [ES93],[Ga99],[Ru99b].

9. Outlook

The subject is (clearly) at a very early stage of development.

(1) The theory can be extended to stochastic thermostats quite satisfactorily, at least as far as the fluctuation theorem is concerned.

(2) Remarkable works have appeared on the theory of systems which are purely Hamiltonian and (therefore) with thermostats that are infinite: unfortunately the infinite thermostats can be treated, so far, only if their particles are “free” at infinity (either free gases or harmonic lattices).

(3) The notion of entropy turns out to be extremely difficult to extend to stationary states and there are even doubts that it could be actually extended. Conceptually this is certainly a major open problem.

(4) The statistical properties of stationary states out of equilibrium are still quite mysterious and surprising: recently appeared exactly solvable models as well as attempts at unveiling the deep reasons for their solubility and at deriving from them general guiding principles.

(5) Numerical simulations have given a strong impulse to the subject, in fact one can even say that they created it: introducing the model of thermostat as an extra microscopic force acting on the particle and providing the first reliable results on the properties of systems out of equilibrium. Simulations continue to be an essential part of the effort of research on the field.

(6) Approach to stationarity leads to many important questions: is there a Lyapunov function measuring the distance between an evolving state and the stationary state towards which it evolves? In other words can one define an analogous of Boltzmann’s H -function? About this question there have been proposals and the answer seems affirmative, but it does not seem that it is possible to find a universal, system independent, such function (search for it is related to the problem of defining an entropy function for stationary states: its existence is at least controversial, see Sec.2,3).

(7) Studying non stationary evolution is much harder. The problem arises when the control parameters (force, volume, ...) change with time and the system *undergoes a process*. As an example one can ask the question of how irreversible is a given *irreversible process* in which the initial state μ_0 is a stationary state and at time $t = 0$ and the external parameters Φ_0 start changing into functions $\Phi(t)$ of t and tend to a limit Φ_∞ as $t \rightarrow \infty$? In this case the stationary distribution μ_0 starts changing and becomes a function μ_t of t which *is not stationary* but approaches another stationary distribution μ_∞ as $t \rightarrow \infty$. The process is, in general, irreversible and the question is how to measure its *degree of irreversibility*: for simplicity we restrict attention to very special processes in which the only phenomenon is heat production because the container does not change volume and the energy remains constant, so that the motion can be described at all times as taking place on a fixed energy surface. A natural quantity \mathcal{I} associated with the evolution from an initial stationary state to a final stationary state through a change in the control parameters can be defined as follows. Consider the distribution μ_t into which μ_0 evolves in time t , and consider also the SRB distribution $\mu_{\Phi(t)}$ corresponding to the control parameters “frozen”

at the value at time t , *i.e.* $\Phi(t)$. Let the phase space contraction, when the forces are “frozen” at the value $\Phi(t)$, be $\sigma_t(x) = \sigma(x; \Phi(t))$. In general $\mu_t \neq \mu_{\Phi(t)}$. Then

$$\mathcal{I}(\{\Phi(t)\}, \mu_0, \mu_\infty) \stackrel{def}{=} \int_0^\infty (\mu_t(\sigma_t) - \mu_{\Phi(t)}(\sigma_t))^2 dt \quad (9.1)$$

can be called the *degree of irreversibility of the process*: it has the property that in the limit of infinitely slow evolution of $\Phi(t)$, *e.g.* if $\Phi(t) = \Phi_0 + (1 - e^{-\gamma\kappa t})\Delta$ (a *quasi static evolution* on time scale $\gamma^{-1}\kappa^{-1}$ from Φ_0 to $\Phi_\infty = \Phi_0 + \Delta$), the irreversibility degree $\mathcal{I}_\gamma \xrightarrow{\gamma \rightarrow 0} 0$ if (as in the case of Anosov evolutions, hence under the chaotic hypothesis) the approach to a stationary state is exponentially fast at fixed external forces Φ . The quantity \mathcal{I}^{-1} is a time scale which could be interpreted as the time needed for the process to exhibit its irreversible nature.

The entire subject is dominated by the initial insights of Onsager on classical nonequilibrium thermodynamics: which concern the properties of the infinitesimal deviations from equilibrium (*i.e.* averages of observables differentiated with respect to the control parameters Φ and evaluated at $\Phi = \mathbf{0}$). The present efforts are devoted to studying properties at $\Phi \neq \mathbf{0}$. In this direction the classical theory provides certainly firm constraints (like Onsager reciprocity or Green-Kubo relations or fluctuation dissipation theorem) but at a technical level it gives little help to enter the *terra incognita* of nonequilibrium thermodynamics of stationary states.

References: [Ku98],[LS99],[Ma99]; [EPR99],[BLR00],[EY05]; [DLS01];[BDGJL01]; [EM90],[ECM33]; [GL03],[Ga04],[BGGZ05].

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