Chapter 2
Stationary Nonequilibrium

2.1 Thermostats and Infinite Models

The essential difference between equilibrium and nonequilibrium is that in the first case time evolution is conservative and Hamiltonian while in the second case time evolution takes place under the action of external agents which could be, for instance, external nonconservative forces.

Nonconservative forces perform work and tend to increase the kinetic energy of the constituent particles: therefore a system subject only to this kind of forces cannot reach a stationary state. For this reason in nonequilibrium problems there must exist other forces which have the effect of extracting energy from the system balancing, in average, the work done or the energy injected on the system.

This is achieved in experiments as well as in theory by adding thermostats to the system. Empirically a thermostat is a device (consisting also of particles, like atoms or molecules) which maintains its own temperature constant while interacting with the system of interest.

In an experimental apparatus thermostats usually consist of large systems whose particles interact with those of the system of interest: so large that, for the duration of the experiment, the heat that they receive from the system affects negligibly their temperature.

However it is clear that locally near the boundary of separation between system and thermostat there will be variations of temperature which will not increase indefinitely, because heat will flow away towards the far boundaries of the thermostats containers. But eventually the temperature of the thermostats will start changing and the experiment will have to be interrupted: so it is necessary that the system reaches a satisfactorily stationary state before the halt of the experiment. This is a situation that can be achieved by suitably large thermostatting systems.

There are two ways to model thermostats. At first the simplest would seem to imagine the system enclosed in a container C_0 in contact, through separating walls, with other containers $\Theta_1, \Theta_2, \ldots, \Theta_n$ as illustrated in Fig. 2.1.

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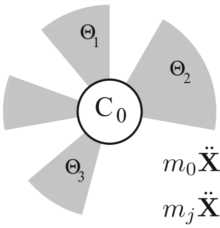


$$\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$$

$$m_0 \ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \textstyle\sum_j \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i(\mathbf{X}_0)$$
$$m_j \ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$$

Fig. 2.1 C_0 represents the system container and Θ_j the thermostats containers whose temperatures are denoted by T_j, $j = 1, \ldots, n$. The thermostats are infinite systems of interacting (or free) particles which at all time are supposed to be distributed, far away from C_0, according to a Gibbs' distribution at temperatures T_j. All containers have elastic walls and $U_j(\mathbf{X}_j)$ are the potential energies of the internal forces while $U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$ is the interaction potential between the particles in C_0 and those in the infinite thermostats

The box C_0 contains the "*system of interest*", or "*test system*" to follow the terminology of the pioneering work by Feynman and Vernon [1], consisting of N_0 particles while the containers labeled $\Theta_1, \ldots, \Theta_n$ are *infinite* and contain particles with average densities $\varrho_1, \varrho_2, \ldots, \varrho_n$ and temperatures at infinity $T_1, T_2, \ldots, T_n$ which constitute the "*thermostats*", or "*interaction systems*" to follow [1]. Positions and velocities are denoted $\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n$, and $\dot{\mathbf{X}}_0, \dot{\mathbf{X}}_1, \ldots, \dot{\mathbf{X}}_n$ respectively, particles masses are $m_0, m_1, \ldots, m_n$. The $\mathbf{E}$ denote external, non conservative, forces.

The temperatures of the thermostats are defined by requiring that initially the particles in each thermostat have an initial distribution which is asymptotically a Gibbs distribution with densities $\rho_1, \ldots, \rho_n$, with inverse temperatures $(k_B T_1)^{-1}, \ldots, (k_B T_n)^{-1}$ and interaction potentials $U_j(\mathbf{X}_j)$ generated by a short range pair potential φ with at least the usual stability properties, [2, Sect. 2.2] i.e. enjoying the lower boundedness property $\sum_{i<j}^{1,n} \varphi(q_i - q_j) \ge -Bn, \forall n$, with $B \ge 0$.

Likewise $U_0(\mathbf{X}_0)$ denotes the potential energy of the pair interactions of the particles in the test system and finally $U_{0,j}(\mathbf{X}_0, \mathbf{X}_j)$ denotes the interaction energy between particles in C_0 and particles in the thermostat Θ_j, also assumed to be generated by a pair potential (e.g. the same φ, for simplicity).

The interaction between thermostats and test system are supposed to be *efficient* in the sense that the work done by the external forces and by the thermostats forces will balance, in the average, and keep the test system within a bounded domain in phase space or at least keep its distribution essentially concentrated on bounded phase space domains with a probability which goes to one, as the radius of the phase space domain tends to infinity, at a time independent rate, thus being compatible with the realization of a stationary state.

The above model, first proposed in [1], in a quantum mechanical context, is a typical model that seems to be accepted widely as a physically sound model for thermostats.

However it is quite unsatisfactory; not because infinite systems are unphysical: after all we are used to consider 10^{19} particles in a container of $1\,\mathrm{cm}^3$ as essentially an infinite system; but because it is very difficult to develop a theory of the motion of infinitely many particles distributed with positive density. So far the cases in which the model has been pushed beyond the definition assume that the systems in the thermostats are free systems, as done already in [1], ("free thermostats").

A further problem with this kind of thermostats that will be called "Newtonian" or "conservative" is that, aside from the cases of free thermostats, they are not suited for simulations. And it is a fact that in the last thirty years or so new ideas and progress in nonequilibrium has come from the results of numerical simulations. However the simulations are performed on systems interacting with *finite thermostats*.

Last but not least a realistic thermostat should be able to maintain a temperature gradient because in a stationary state only the temperature at infinity can be exactly constant: in infinite space this is impossible if the space dimension is 1 or 2.[1]

2.2 Finite Thermostats

The simplest finite thermostat models can be illustrated in a similar way to that used in Fig. 2.1:

The difference with respect to the previous model is that the containers $\Theta_1, \ldots, \Theta_n$ are now *finite*, obtained by bounding the thermostats containers at distance ℓ from the origin, by adding a spherical elastic boundary Ω_ℓ of radius ℓ (for definiteness), and contain $N_1, \ldots, N_n$ particles.

The condition that the thermostats temperatures should be fixed is imposed by imagining that there is an extra force $-\alpha_j \dot{\mathbf{X}}_j$ acting on all particles of the j-th thermostat and the multipliers α_j are so defined that the kinetic energies $K_j = \frac{m_j}{2}\dot{\mathbf{X}}_j^2$ are exact constants of motion with values $K_j \stackrel{def}{=} \frac{3}{2} N_j k_B T_j, k_B =$ Boltzmann's constant, $j = 1, \ldots, n$. The multipliers α_j are then found to be[2]:

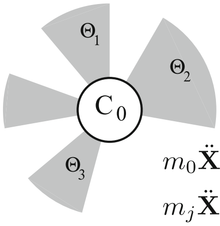
$$\alpha_j = -\frac{(Q_j + \dot{U}_j)}{3N_j k_B T_j} \qquad \text{with} \quad Q_j \stackrel{def}{=} -\dot{\mathbf{X}}_j \cdot \partial_{\mathbf{X}_j} U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) \tag{2.2.1}$$

where Q_j, which is the work per unit time performed by the particles in the test system upon those in the container Θ_j, is naturally interpreted as the *heat* ceded per unit time to the thermostat Θ_j.

The energies $U_0, U_j, U_{0,j}$, $j > 0$, should be imagined as generated by pair potentials $\varphi_0, \varphi_j, \varphi_{0,j}$ short ranged, stable, smooth, or with a singularity like a hard core or a high power of the inverse distance, and by external potentials generating (or modeling) the containers walls.

[1] Because heuristically it is tempting to suppose that temperature should be defined in a stationary state and should tend to the value at infinity following a kind of heat equation: but the heat equation does not have bounded solutions in an infinite domain, like an hyperboloid, with different values at points tending to infinity in different directions *if the dimension of the container is* 1 *or* 2.

[2] Simply multiplying the both sides of each equation in Fig. 2.2 by $\dot{\mathbf{X}}_j$ and imposing, for each $j = 1, \ldots, n$, that the *r.h.s.* vanishes.



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

$$m_0 \ddot{\mathbf{X}}_{0i} = -\partial_i U_0(\mathbf{X}_0) - \sum_j \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) + \mathbf{E}_i(\mathbf{X}_0)$$
$$m_j \ddot{\mathbf{X}}_{ji} = -\partial_i U_j(\mathbf{X}_j) - \partial_i U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) - \alpha_j \dot{\mathbf{X}}_{ji}$$

Fig. 2.2 Finite thermostats model (Gaussian thermostats): the containers Θ_j are finite and contain N_j particles. The thermostatting effect is modeled by an extra force $-\alpha_j \dot{\mathbf{X}}_j$ so defined that the *total* kinetic energies $K_j = m_j/2\dot{\mathbf{X}}_j^2$ are exact constants of motion with values $K_j \stackrel{def}{=} 3/2 N_j k_B T_j$

One can also imagine that thermostat forces act in like manner within the system in C_0: i.e. there is an extra force $-\alpha_0 \dot{\mathbf{X}}_0$ which also keeps the kinetic energy K_0 constant ($K_0 \stackrel{def}{=} N_0 \frac{3}{2} k_B T_0$), which could be called an “autothermostat” force on the test system. This is relevant in several physically important problems: for instance in electric conduction models the thermostatting is due to the interaction of the electricity carriers with the oscillations (phonons) of an underlying lattice, and the latter can be modeled (if the masses of the lattice atoms are much larger than those of the carriers) [3] by a force keeping the total kinetic energy (i.e. temperature) of the carriers constant. In this case the multiplier α_0 would be defined by

$$\alpha_0 = \frac{(Q_0 + \dot{U}_0)}{3N_0 k_B T_0} \qquad \text{with} \quad Q_0 \stackrel{def}{=} -\sum_{j>0} \dot{\mathbf{X}}_0 \cdot \partial_{\mathbf{X}_j} U_{0,j}(\mathbf{X}_0, \mathbf{X}_j) \tag{2.2.2}$$

Certainly there are other models of thermostats that can be envisioned: all, including the above, were conceived in order to make possible numerical simulations. The first ones have been the “Nosé-Hoover” thermostats, [4–6]. However they are not really different from the above, or from the similar model in which the multipliers α_j are fixed so that the total energy $K_j + U_j$ in each thermostat is a constant; in the latter, for instance, Q_j is defined as in Eq. (2.2.1)

$$\alpha_j = \frac{Q_j}{3N_j k_B T_j}, \qquad k_B T_j \stackrel{def}{=} \frac{2}{3} \frac{K_j}{N_j} \tag{2.2.3}$$

Such thermostats will be called *Gaussian isokinetic* if $K_j = const$, $j \geq 1$, (hence $\alpha_j = (Q_j + \dot{U}_j)/3N_j k_B T_j$, Eq. (2.2.1) or *Gaussian isoenergetic* if $K_j + U_j = const$ (hence $\alpha_j = Q_j/3N_j k_B T_j$, Eq. (2.2.3).

It is interesting to keep in mind the reason for the attribute “Gaussian” to the models. It is due to the interpretation of the constancy of the kinetic energies K_j or of the total energies $K_j + U_j$, respectively, as a *non holonomic constraint* imposed on the particles. Gauss had proposed to call *ideal* the constraints realized by forces satisfying his principle of *least constraint* and the forces $-\alpha_j \dot{\mathbf{X}}_j$, Eq. (2.2.1) or

(2.2.3), do satisfy the prescription. For completeness the principle is reminded in Appendix E. Here I shall mainly concentrate the attention on the latter Newtonian or Gaussian thermostats.

Remark It has also to be remarked that the Gaussian thermostats generate a *reversible dynamics*: this is *very important* as it shows that Gaussian thermostats do not miss the *essential feature of Newtonian mechanics which is the time reversal symmetry*. Time reversal is a symmetry of nature and any model pretending to be close or equivalent to a faithful representation of nature must enjoy the same symmetry.

Of course it will be important to focus on results and properties which

(1) Have a physical interpretation,
(2) Do not depend on the thermostat model, at least if the numbers of particles $N_0, N_1, \ldots, N_n$ are large.

The above view of the thermostats and the idea that purely Hamiltonian (but infinite) thermostats can be represented equivalently by finite Gaussian termostats external to the system of interest is clearly stated in [7], which precedes the similar [8]

2.3 Examples of Nonequilibrium Problems

Some interesting concrete examples of nonequilibrium systems are illustrated in the following figure (Fig. 2.3).

The multiplier α is $\alpha = \mathbf{E} \cdot \dot{\mathbf{x}}/Nm\dot{\mathbf{x}}^2$ and this is an electric conduction model of N charged particles ($N = 2$ in the figure) in a constant electric field $\mathbf{E}$ and interacting with a lattice of obstacles; it is "autotermostatted" (because the particles in the container C_0 do not have contact with any "external" thermostat). This is a model that appeared since the early days (Drude 1899, [9, Vol. 2, Sect. 35]) in a slightly different form (i.e. in dimension 3, with point particles and with the thermostatting realized by replacing the $-\alpha\dot{\mathbf{x}}$ force with the prescription that after collision of a particle with an obstacle its velocity is rescaled to $|\dot{\mathbf{x}}| = \sqrt{\frac{3}{m}k_B T}$). The thermostat

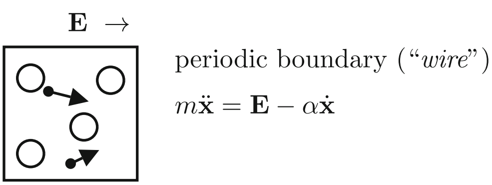


Fig. 2.3 A model for electric conduction. The container C_0 is a box with opposite sides identified (periodic boundary). N particles, hard disks ($N = 2$ in the figure), collide elastically with each other and with other fixed hard disks: the mobile particles represent electricity carriers subject also to an electromotive force E; the fixed disks model an underlying lattice whose phonons are phenomenologically represented by the force $-\alpha\dot{\mathbf{x}}$. This is an example of an autothermostatted system in the sense of Sect. 2.2

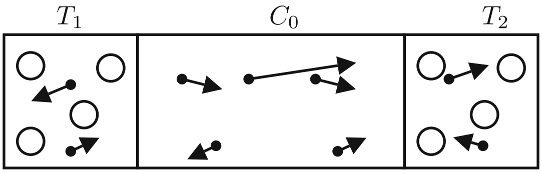


Fig. 2.4 A model for thermal conduction in a gas: particles in the central container C_0 are N_0 hard disks and the particles in the two thermostats are also hard disks; collisions occur whenever the centers of two disks are at distance equal to their diameters. Collisions with the separating walls or bounding walls occur when the disks centers reach them. All collisions are elastic. Inside the two thermostats act thermostatic forces modeled by $-\alpha_j \dot{\mathbf{X}}_j$ with the multipliers α_j, $j = 1, 2$, such that the total kinetic energies in the two boxes are constants of motion $K_j = \frac{N_j}{2} k_B T_j$. If a constant force E acts in the *vertical* direction and the *upper* and *lower* walls of the central container are identified, while the corresponding walls in the *lateral* boxes are reflecting (to break momentum conservation), then this becomes a model for electric and thermal conduction in a gas

forces are a model of the effect of the interactions between the particle (electron) and a background lattice (phonons). This model is remarkable because it is the first nonequilibrium problem that has been treated with real mathematical attention and for which the analog of Ohm's law for electric conduction has been (recently) proved if $N = 1$, [10]

Another example is a model of thermal conduction, Fig. 2.4:

In the model N_0 hard disks interact by elastic collisions with each other and with other hard disks ($N_1 = N_2$ in number) in the containers labeled by their temperatures T_1, T_2: the latter are subject to elastic collisions between themselves and with the disks in the central container C_0; the separations reflect elastically the particles when *their centers* touch them, thus allowing interactions between the thermostats and the main container particles. Interactions with the thermostats take place only near the separating walls.

If one imagines that the upper and lower walls of the *central* container are identified (realizing a periodic boundary condition)[3] and that a constant field of intensity E acts in the vertical direction then two forces conspire to keep it out of equilibrium, and the parameters $\mathbf{F} = (T_2 - T_1, E)$ characterize their strength: matter and heat currents flow.

The case $T_1 = T_2$ has been studied in simulations to check that the thermostats are "efficient" at least in the few cases examined: i.e. that the simple interaction, via collisions taking place across the boundary, is sufficient to allow the systems to reach a stationary state, [11]. A mathematical proof of the above efficiency (at $E \neq 0$), however, seems very difficult (and desirable).

To insure that the system and thermostats can reach a stationary state a further thermostat could be added $-\alpha_0 \dot{\mathbf{X}}_0$ that keeps the total kinetic energy K_0 constant

[3] Reflecting boundary conditions on all walls of the side thermostat boxes are imposed to avoid that a current would be induced by the collisions of the "flowing" particles in the central container with the thermostats particles.

and equal to some $\frac{3}{2}N_0 k_B T_0$: this would model a situation in which the particles in the central container exchange heat with a background at temperature T_0. This autothermotatted case has been considered in simulations in [3].

2.4 Initial Data

Any set of observations starts with a system in a state x in phase space prepared by some well defined procedure. In nonequilibrium problems systems are always large, because the thermostats and, often, the test system are always supposed to contain many particles: therefore any physically realizable preparation procedure will not produce, upon repetition, the same initial state.

It is a basic assumption that whatever physically realizable preparation procedure is employed it will produce initial data which have a random probability distribution which has a density in the region of phase space allowed by the external constraints. This means, for instance, that in the finite model in Sect. 2.2 the initial data could be selected randomly with a distribution of the form

$$\mu_0(dx) = \varrho(x) \prod_{j=1}^{n} \delta(K_j, T_j) \prod_{j=0}^{n} d\mathbf{X}_j d\dot{\mathbf{X}}_j \tag{2.4.1}$$

where $x = (\mathbf{X}_0, \mathbf{X}_1, \ldots, \mathbf{X}_n)$ and $\delta(K_j, T_j) = \delta(K_j - \frac{3}{2}N_j k_B T_j)$ and ϱ is a bounded function on phase space.

If observations are performed at timed events, see Sect. 1.1, and are described by a map $S : \Xi \to \Xi$ on a section Ξ of phase space then Eq. (2.4.1) is replaced by

$$\mu_0(dx) = \varrho(x)\, \delta_\Xi(x) \prod_{j=1}^{n} \delta(K_j, T_j) \prod_{j=0}^{n} d\mathbf{X}_j d\dot{\mathbf{X}}_j \tag{2.4.2}$$

where $\delta_\Xi(x)$ is the delta function imposing that the point x is a timing event, i.e. $x \in \Xi$.

The assumption about the initial data is very important and should not be considered lightly. Mechanical systems as complex as systems of many point particles interacting via short range pair potentials will, *in general*, admit *uncountably many* probability distributions μ which are invariant, hence stationary, under time evolution i.e. such that for all measurable sets $V \subset \Xi$,

$$\mu\Big(S^{-1}V\Big) = \mu(V) \tag{2.4.3}$$

where S is the evolution map and "measurable" means any set that can be obtained by a countable number of operations of union, complementation and intersection from the open sets, i.e. *any reasonable set*. In the continuous time representation Ξ is replaced by the full phase space X and the invariance condition becomes $\mu(S_{-t}W) = \mu(W)$ for all $t > 0$ and all measurable sets W.

In the case of infinite Newtonian thermostats the random choice with respect to μ_0 in Eq. (2.4.1) will be with x being chosen with the Gibbs distribution $\mu_{G,0}$ *formally*, [2], given by

$$\mu_{G,0}(dx) = const\, e^{-\sum_{j=0}^{n}\beta_j\left(K_j+U_j\right)} dx \tag{2.4.4}$$

with $\beta_j^{-1} = k_B T_j$ and some average densities ϱ_j assigned to the particles in the thermostats: satisfying the initial condition of assigning to the configurations in each thermostat the temperature T_j and the densities ϱ_j, but obviously not invariant.[4]

To compare the evolutions in infinite Newtonian thermostats and in large Gaussian thermostats it is natural to choose the initial data in a consistent way (i.e. coincident) in the two cases. Hence in both cases (Newtonian and Gaussian) it will be natural to choose the data with the same distribution $\mu_{G,0}(dx)$, Eq. (2.4.4), and imagine that in the Gaussian case the particles *outside* the finite region, bounded by a reflecting sphere Ω_ℓ of radius ℓ, occupied by the thermostats the particles are "frozen" in the initial positions and velocities of x.

In both cases the initial data can be said to have been chosen respecting the constraints (at given densities and temperatures).

Assuming that physically interesting initial data are generated on phase space M by the above probability distributions $\mu_{G,0}$, Eq. (2.4.4), (or any distribution with density with respect to $\mu_{G,0}$) means that the invariant probability distributions μ that we consider *physically relevant* and that can possibly describe the statistical properties of stationary states are the ones that can be obtained as limits of time averages of iterates of distributions $\mu_{G,0}$. More precisely, in the continuous time cases,

$$\mu(F) = \lim_{\tau\to\infty}\frac{1}{\tau}\int_0^\tau dt\int_M \mu_{G,0}(dx)F(S_t x) \tag{2.4.5}$$

or, in the discrete time cases:

$$\mu(F) = \lim_{k\to\infty}\frac{1}{k}\sum_{q=0}^{k-1}\int_\Xi \delta_\Xi(x)\mu_{G,0}(dx)F(S^q x) \tag{2.4.6}$$

[4] Not even if $\beta_j = \beta$ for all $j = 0, 1, \ldots, n$ because the interaction between the thermostats and the test system are ignored. In other words the initial data are chosen as independently distributed in the various thermostats and in the test system with a canonical distribution in the finite test system and a Gibbs distribution in the infinite reservoirs case. Of course any distribution with a density with respect to $\mu_{G,0}$ will be equivalent to it, for our purposes.

for all continuous observables F on the test system,[5] where possibly the limits ought to be considered over subsequences (which do not depend on F).

It is convenient to formalize the above analysis, to underline the specificity of the assumption on the initial data, into the following:

Initial data hypothesis *In a finite mechanical system the stationary states correspond to invariant probability distributions μ which are time averages of probability distributions which have a density on the part of phase space compatible with the constraints.*

The assumption, *therefore*, declares "unphysical" the invariant probability distributions that are not generated in the above described way. It puts very severe restriction on which could possibly be the statistical properties of nonequilibrium or equilibrium states.[6]

In general stationary states obtained from initial data chosen with distributions which have a density as above are called SRB distributions. They are not necessarily unique although they are unique in important cases, see Sect. 2.6.

The physical importance of the choice of the initial data in relation to the study of stationary states has been proposed, stressed and formalized by Ruelle, [12–15].

For instance if a system is in equilibrium, i.e. no nonconservative forces act on it and all thermostats are Gaussian and have equal temperatures, then the limits in Eqs. (2.4.5), (2.4.6) are usually supposed to exist, to be ϱ independent and to be equivalent to the Gibbs distribution. Hence the distribution μ has to be

$$\mu(dx) = \frac{1}{Z} e^{-\beta\left(\sum_{j=0}^{n} U_j(\mathbf{X}_j)+\sum_{j=1}^{n} W_j(\mathbf{X}_0,\mathbf{X}_j)\right)} \prod_{j=1}^{n} \delta(K_j, T) \prod_{j=0}^{n} d\mathbf{X}_j\, d\dot{\mathbf{X}}_j \quad (2.4.7)$$

where $\beta = 1/k_B T$, $T_j \equiv T$ and $\delta(K_j, T)$ has been defined after Eq. (2.4.1), provided μ is unique within the class of initial data considered.

In nonequilibrium systems there is the possibility that asymptotically motions are controlled by several attracting sets, typically in a finite number, i.e. closed and disjoint sets $\mathcal{A}$ such that points x close enough to $\mathcal{A}$ evolve at time t into $x(t)$ with distance of $x(t)$ from $\mathcal{A}$ tending to 0 as $t \to \infty$. Then the limits above are not expected to be unique unless the densities ϱ are concentrated close enough to one of the attracting sets.

Finally a warning is necessary: in special cases the preparation of the initial data is, out of purpose or of necessity, such that with probability 1 it produces data which lie in a set of 0 phase space volume, hence of vanishing probability with respect to

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[5] i.e. depending only on the particles positions and momenta inside $\mathcal{C}_0$, or more generally, within a finite ball centered at a point in $\mathcal{C}_0$.

[6] In the case of Newtonian thermostats, i.e. infinite, the probability distributions to consider for the choice of the initial data are naturally the above $\mu_{G,0}$, Eq. (2.4.5) or distributions with density with respect to them.

μ_0, Eq. (2.4.2), or to any probability distribution with density with respect to volume of phase space. In this case, *of course*, the initial data hypothesis above does not apply: the averages will still exist quite generally but the corresponding stationary state will be different from the one associated with data chosen with a distribution with density with respect to the volume. Examples are easy to construct as it will be discussed in Sect. 3.9 below.

2.5 Finite or Infinite Thermostats? Equivalence?

In the following we shall choose to study *finite* thermostats.

It is clear that this can be of any interest only if the results can, in some convincing way, be related to thermostats in which particles interact via Newtonian forces.

As said in Sect. 2.1 the only way to obtain thermostats of this type is to make them infinite: because the work Q that the test system performs per unit time over the thermostats (heat ceded to the thermostats) will change the kinetic energy of the thermostats and the only way to avoid indefinite heating (or cooling) is that the heat flows away towards (or from) infinity, hence the necessity of infinite thermostats. Newtonian forces and finite thermostats will result eventually in an equilibrium state in which all thermostats temperatures have become equal.

Therefore it becomes important to establish a relation between infinite Newtonian thermostats with only conservative, short range and stable pair forces and finite Gaussian thermostats with additional *ad hoc* forces, as the cases illustrated in Sect. 2.2.

Probably the first objection is that a relation seems doubtful because the equations of motion, and therefore the motions, are different in the two cases. Hence a first step would be to show that *instead* in the two cases the motions of the particles are very close at least if the particles are in, or close to, the test system and the finite thermostats are large enough.

A heuristic argument is that the non Newtonian forces $-\alpha_i \dot{\mathbf{X}}_j$, Eq. (2.2.1), are proportional to the inverse of the number of particles N_j while the other factors (i.e Q_j and $\dot{U}_j$) are expected to be of order $O(1)$ being proportional to the number of particles present in a layer of size twice the interparticle interaction range: hence in large systems their effect should be small (and zero in the limits $N_j \to \infty$ of infinite thermostats). This has been discussed, in the case of a single self-thermostatted test system, in [16], and more generally in [7], accompanied by simulations.

It is possible to go quite beyond a theoretical heuristic argument. However this requires first establishing existence and properties of the dynamics of systems of infinitely many particles. This can be done as described below.

The best that can be hoped is that initial data $\dot{\mathbf{X}}, \mathbf{X}$ chosen randomly with a distribution $\mu_{0,G}$, Eq. (2.4.5), which is a Gibbs distribution with given temperatures and density for the infinitely many particles in each thermostat and with any density for the finitely many particles in the test system, will generate a solution of the equations in Fig. 2.1 with the added prescription of elastic reflection by the boundaries (of the test system and of the thermostats), i.e. a $\dot{\mathbf{X}}(t), \mathbf{X}(t)$ for which both sides of the equation make sense and are equal for all times $t \geq 0$, *with the exception of a set of initial data which has* 0 $\mu_{0,G}$*-probability*.

At least in the case in which the interaction potentials are smooth, repulsive and short range such a result can be proved, [17–19] in the geometry of Fig. 2.1 in space dimension 2 and in at least one special case of the same geometry in space dimension 3.

If initial data $x = \big(\dot{\mathbf{X}}(0), \mathbf{X}(0)\big)$ are chosen randomly with the probability $\mu_{G,0}$ the equation in Fig. 2.1 admits a solution $x(t)$, with coordinates of each particle smooth functions of t.

Furthermore, in the same references considered, the finite Gaussian thermostats model, *either isokinetic or isoenergetic*, is realized in the geometry of Fig. 2.2 by terminating the thermostats containers within a spherical surface Ω_ℓ of radius $\ell = 2^k R$, with R being the linear size of the test system and $k \geq 1$ integer.

Imagining the particles external to the ball Ω_ℓ to keep positions and velocities "frozen" in time, the evolution of the particles inside Ω_ℓ will be defined adding to the interparticle forces elastic reflections on the spherical boundaries of Ω_ℓ and the other boundaries of the thermostats and of the test system. It will therefore follow a finite number of ordinary differential equations and at time t the initial data $x = (\dot{\mathbf{X}}(0), \mathbf{X}(0))$, if chosen randomly with respect to the distribution $\mu_{G,0}$ in Eq. (2.4.5), will be transformed into $\dot{\mathbf{X}}^{[k]}(t), \mathbf{X}^{[k]}(t)$ (depending on the regularization parameter $\ell = 2^k R$ and on the isokinetic or isoenergetic nature of the thermostatting forces). Then it is possible to prove the property:

Theorem *Fixed arbitrarily a time* $t_0 > 0$ *there exist two constants* $C, c > 0$ *(*t_0 *–dependent) such that the isokinetic or isoenergetic motions* $x_j^{[k]}(t)$ *are related as:*

$$|x_j(t) - x_j^{[k]}(t)| \leq Ce^{-c2^k}, \qquad \text{if } |x_j(0)| < 2^{k-1}R \tag{2.5.1}$$

for all $t \leq t_0,\ j$*, with* μ_0*-probability* 1 *with respect to the choice of the initial data.*

In other words the Newtonian motion and the Gaussian thermostatted motions become rapidly indistinguishable, up to a prefixed time t_0, if the thermostats are large (k large) and if we look at particles initially located within a ball half the size of the confining sphere of radius $\ell = 2^k R$, where the spherical thermostats boundaries are located, i.e. within the ball of radius $2^{k-1}R$.

This theorem is only a beginning, although in the right direction, as one would really like to prove that the evolution of the initial distribution μ_0 lead to a stationary distribution in both cases and that the stationary distributions for the Newtonian and the Gaussian thermostats *coincide in the "thermodynamic limit"* $k \to \infty$.

At this point a key observation has to be made: it is to be expected that in the thermodynamic limit once a stationary state is reached starting from $\mu_{G,0}$ the thermostats temperature (to be suitably defined) should appear varying smoothly toward a value at infinity, in each thermostat Θ_j, equal to the initially prescribed temperature (appearing in the random selection of the initial data with the given distribution $\mu_{G,0}$, Eq. 2.4.5).

Hence the temperature variation should be described, at least approximately, by a solution of the heat equation $\Delta T(q) = 0$ and $T(q)$ not constant, bounded, with Neumann's boundary condition $\partial_n T = 0$ on the lateral boundary of the container $\Omega_\infty = \lim_{\ell\to\infty} \Omega_\ell$ and tending to T_j as $q \in \Theta_j$, $q \to \infty$. However if the space dimension is 1 or 2 there is no such harmonic function.

Therefore the systems considered should be expected to behave as our three dimensional intuition commands only if the space dimension is 3 (or more): it can be expected that the stationary states of the two thermostats models become equal in the thermodynamic limit only if the space dimension is 3.

It is interesting that if really equivalence between the Newtonian and Gaussian thermostats could be shown then the average of the mechanical observable $\sum_{j=1}^{n} 3N_j\alpha_j$, naturally interpreted in the Gaussian case in Eq. (2.2.1), (2.2.3) as entropy production rate, would make sense as an observable also in the Newtonian case[7] with no reference to the thermostats and will have the same average: so that the equivalence makes clear that it *is possible that a Newtonian evolution produces entropy*. *I.e.* entropy production is compatible with the time reversibility of Newton's equations [7].

2.6 SRB Distributions

The limit probability distributions in Eqs. (2.4.5), (2.4.6) are called *SRB distributions*, from Sinai, Ruelle, Bowen who investigated, and solved in important cases, [20–22], the more difficult question of finding conditions under which, for motions in continuous time on a manifold M, the following limits

$$\lim_{\tau\to\infty} \frac{1}{\tau} \int_0^t F(S_t x)\, dt = \int_X F(y)\mu(dy) \tag{2.6.1}$$

exist for all continuous observables F, and *for all* $x \in M$ chosen randomly according to the initial data hypothesis (Sect. 2.4).[8] A question that in timed observations becomes finding conditions under which, for all continuous observables F, the following limits

$$\lim_{\tau\to\infty} \frac{1}{k} \sum_{q=0}^{k-1} F(S^k x)\, dt = \int_\Xi F(y)\mu(dy) \tag{2.6.2}$$

[7] Because the *r.h.s.* in the quoted formulae are expressed in terms of mechanical quantities $Q_j, \dot{U}_j$ and the temperatures at infinity T_j.

[8] i.e. except possibly for a set V_0 of data x which have zero probability in a distribution with density with respect to the volume and concentrated close enough to an attracting set.

exist *for all* $x \in \Xi$ chosen randomly according to the initial data hypothesis and close enough to an attracting set.

The Eqs. (2.6.1), (2.6.2) express properties stronger than those in the above Eqs. (2.4.5), (2.4.6): no subsequences and no average over the initial data.

Existence of the limits above, outside a set of 0 volume, can be established for systems which are *smooth, hyperbolic and transitive*, also called *Anosov systems* or systems with the *Anosov property*. In the case of *discrete time evolution map* the property is:

Definition (*Anosov map*) Phase space Ξ is a smooth bounded ("compact") Riemannian manifold and evolution is given by a smooth map S with the properties that an infinitesimal displacement dx of a point $x \in \Xi$

(1) Can be decomposed as sum $dx^s + dx^u$ of its components along two transverse planes $V^s(x)$ and $V^u(x)$ which depend continuously on x
(2) $V^\alpha(x)$, $\alpha = u, s$, are covariant under time evolution, in the sense that $(\partial S)(x)V^\alpha(x) = V^\alpha(Sx)$, with $\partial S(x)$ the linearization at x of S ("Jacobian matrix")
(3) Under iteration of the evolution map the vectors dx^s contract exponentially fast in time while the vectors dx^u expand exponentially: in the sense that $|\partial S^k(x)dx^s| \le Ce^{-\lambda k}|dx^s|$ *and* $|\partial S^{-k}(x)dx^u| \le Ce^{-\lambda k}|dx^u|$, $k \ge 0$, for some x-independent $C, \lambda > 0$.
(4) There is a point x with a dense trajectory ("transitivity").

Here ∂S^k denoted the Jacobian matrix $\frac{\partial S^k(x)_i}{\partial x_j}$ of the map S^k at x. Thus $\partial S^k(x)dx$ is an infinitesimal displacement of $S^n x$ and the lengths $|dx^\alpha|$ and $|\partial S^k(x)dx^\alpha|$, $\alpha = s, u$, are evaluated through the metric of the manifold Ξ at the points x and $S^k x$ respectively.

Anosov maps have many properties which will be discussed in the following and that make the evolutions associated with such maps a paradigm of chaotic motions. For the moment we just mention a remarkable property, namely

Theorem (SRB)[9] *If S is a Anosov map on a manifold then there exists a unique probability distribution μ on phase space Ξ such that for all choices of the density $\varrho(x)$ defined on Ξ the limits in Eq.* (2.6.2) *exist for all continuous observables F and for all x outside a zero volume set.*

Given the assumption on the initial data it follows that in Anosov systems the probability distributions that give the statistical properties of the stationary states are uniquely determined as functions of the parameters on which S depends.

For evolutions on a smooth bounded manifold M *developing in continuous time* there is an analogous definition of "Anosov flow". For obvious reasons the infinitesimal displacements dx pointing in the flow direction cannot expand nor contract with time: hence the generic dx will be covariantly decomposed as a sum $dx^s + dx^u + dx^0$ with dx^s, dx^u exponentially contracting under S_t: in the sense that for some C, λ

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[9] SRB stands for Sinai-Ruelle-Bowen [14].

it is $|\partial S_t dx^s| \le Ce^{-\lambda t}|dx^s|$ and $|\partial S_{-t} dx^u| \le Ce^{-\lambda t}|dx^u|$ as $t \to +\infty$, while (of course) $|\partial S_t dx^0| \le C|dx^0|$ as $t \to \pm\infty$; furthermore there is a dense orbit and there is no τ such that the map S^n_τ admits a non trivial constant of motion.[10] Then the above theorem holds without change replacing in its text Eq. (2.6.2) by Eq. (2.6.1), [22–24].

2.7 Chaotic Hypothesis

The latter mathematical results on Anosov maps and flows suggest a daring assumption inspired by the certainly daring assumption that all motions are periodic, used by Boltzmann and Clausius to discover the relation between the action principle and the second principle of thermodynamics, see Sect. 1.3.

The assumption is an interpretation of a similar proposal advanced by Ruelle, [12], in the context of the theory of turbulence. It has been proposed in [25] and called "*chaotic hypothesis*". For empirically chaotic evolutions, given by a map S on a phase space Ξ, or for continuous time flows S_t on a manifold M, it can be formulated as

Chaotic hypothesis *The evolution map S restricted to an attracting set $\mathcal{A} \subset \Xi$ can be regarded as an Anosov map for the purpose of studying statistical properties of the evolution in the stationary states.*

This means that attracting sets $\mathcal{A}$ can be considered "for practical purposes" as smooth surfaces on which the evolution map S or flow S_t has the properties that characterize the Anosov maps. It follows that

Theorem *Under the chaotic hypothesis initial data chosen with a probability distribution with a density ϱ on phase space concentrated near an attracting set $\mathcal{A}$ evolve so that the limit in Eqs.* (2.6.1) or (2.6.2) exists for all initial data x *aside a set of zero probability and for all smooth F and are given by the integrals of F with respect to a unique invariant probability distribution μ defined on $\mathcal{A}$.*

This still holds under much weaker assumptions which, however, will not be discussed given the purely heuristic role that will be played by the chaotic hypothesis.[11]

As the ergodic hypothesis is used to justify using the distributions of the microcanonical ensemble to compute the statistical properties of the equilibrium states and to realize the mechanical interpretation of the heat theorem (i.e. existence of the

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[10] The last condition excludes evolutions like $S_t(x, \varphi) = (Sx, \varphi + t)$, or reducible to this form after a change of variables, with S an Anosov map and $\varphi \in [0, 2\pi]$ and angle, i.e. the most naive flows for which the condition does not hold are also the only cases in which the theorem statement would fail.

[11] For instance if the attracting set satisfies the property "Axiom A", [14, 26], the above theorem holds as well as the key results, presented in the following, on existence of Markov partitions, coarse graining and fluctuation theorem which are what is really wanted for our purposes, see Sects. 3.3, 3.7, 4.6. The heroic efforts mentioned in the footnote[2] of the preface reflect a misunderstanding of the physical meaning of the chaotic hypothesis.

entropy function), likewise the chaotic hypothesis will be used to infer the nature of the probability distributions that describe the statistical properties of the more general stationary nonequilibrium states.

This is a nontrivial task as it will be soon realized, see next section, that in general in nonequilibrium the probability distribution μ will have to be concentrated on a set of zero volume in phase space, *even when the attracting sets coincide with the whole phase space*.

In the case in which the volume is conserved, e.g. in the Hamiltonian Anosov case, *the chaotic hypothesis implies the ergodic hypothesis*: which is important because this shows that assuming the new hypothesis cannot lead to a contradiction between equilibrium and nonequilibrium statistical mechanics. The hypothesis name has been chosen precisely because of its assonance with the ergodic hypothesis of which it is regarded here as an extension.

2.8 Phase Space Contraction in Continuous Time

Understanding why the stationary distributions for systems in nonequilibrium are concentrated on sets of zero volume is the same as realizing that the volume (generically) contracts under non Hamiltonian time evolution.

If we consider the measure $dx = \prod_{j=0}^{n} d\mathbf{X}_j\, d\dot{\mathbf{X}}_j$ on phase space then, under the time evolution in continuous time, the volume element dx is changed into $S_t dx$ and the rate of change at $t = 0$ of the volume dx per unit time is given by the divergence of the equations of motion, which we denote $-\sigma(x)$. Given the equations of motion the divergence can be computed: for instance in the model in Fig. 2.2, i.e. an isoenergetic Gaussian thermostats model, and $K_j \stackrel{def}{=} 1/2\dot{\mathbf{X}}_j^2$ is the total kinetic energy in the j-th thermostat, it is (Eq. 2.2.3)[12]:

$$\sigma(x) = \sum_{j>0} \frac{Q_j}{k_B T_j}, \quad Q_j = -\partial_{\mathbf{X}_j} W_j(\mathbf{X}_0, \mathbf{X}_j) \cdot \dot{\mathbf{X}}_j, \quad N_j k_B T_j \stackrel{def}{=} \frac{2}{3} K_j \qquad (2.8.1)$$

The expression of σ, that will be called the *phase space contraction rate* of the Liouville volume, has the interesting feature that Q_j can be naturally interpreted as the heat that the reservoirs receive per unit time, therefore the phase space contraction contains a contribution that can be identified as the entropy production per unit time.[13]

[12] Here a factor $(1 - 2/N_j)$ is dropped from each addend. Keeping it would cause only notational difficulties and eventually it would have to be dropped on the grounds that the number of particles N_j is very large.

[13] In the Gaussian isokinetic thermostats Q_j has to be replaced by $Q_j + \dot{U}_j$, Eq. (2.2.1). Notice that this is true (always neglecting a factor $O(1/N)$ as in the previous footnote) in spite of the fact that the kinetic energy K_j is not constant in this case: this can be checked by direct calculation or by remarking that α_j is a homogeneous function of degree -1 in the velocities.

Note that the name is justified *without any need to extend the notion of entropy to nonequilibrium situations*: the thermostats keep the same temperature all along and are regarded as systems in equilibrium (in which entropy is a well defined notion).

In the isokinetic thermostat case σ may contain a further term equal to $\frac{d}{dt}\sum_{j>0} U_j/k_BT_j$ which forbids us to give the naive interpretation of entropy production rate to the phase space contraction. To proceed it has to be remarked that the above σ *is not really unambiguously defined.*

In fact the notion of phase space contraction depends on what we call volume: for instance if we use as volume element

$$\mu_0(dx) = e^{-\beta\left(K_0+U_0+\sum_{j=1}^n\left(U_j+W_j(\mathbf{X}_0,\mathbf{X}_j)\right)\right)} \prod_{j=1}^n \delta(K_j,T_j)\prod_{j=0}^n d\mathbf{X}_j d\dot{\mathbf{X}}_j \quad (2.8.2)$$

with $\beta = 1/k_BT > 0$, arbitrary, the variation rate $-\sigma'(x)$ of a volume element is different; if we call $-\beta H_0(x)$ the argument of the exponential, the new contraction rate is $\sigma'(x) = \sigma(x) + \beta\dot{H}_0(x)$ where $\dot{H}_0$ has to be evaluated via the equations of motion so that $\dot{H}_0 = -\sum \alpha_j\dot{\mathbf{X}}_0^2 + E(\mathbf{X}_0)\cdot\dot{\mathbf{X}}_0$ and therefore

$$\sigma'(x) = \sum_{j>0}\frac{Q_j}{k_BT_j} + \frac{d}{dt}D(x) \quad (2.8.3)$$

where D is a suitable observable (in the example $D = \beta H_0(x)$).

The example shows a special case of the *general property* that if the volume is measured using a different density or a different Riemannian metric on phase space the new volume contracts at a rate differing form the original one by a *time derivative* of some function on phase space.

In other words $\sum_{j>0} Q_j/k_BT_j$ does not depend, in the cases considered, on the system of coordinates while D does *but it has* 0 *time average*.

An immediate consequence is that σ should be considered as defined *up to a time derivative* and therefore only its time averages over long times can possibly have a physical meaning: the limit as $\tau \to \infty$ of

$$\langle\sigma\rangle_\tau \stackrel{def}{=} \frac{1}{\tau}\int_0^\tau \sigma(S_tx)dt \quad (2.8.4)$$

is independent of the metric and the density used to define the measure of the volume elements; it might still depend on x.

In the timed evolution the time $\tau(x)$ between successive timing events x and $S_{\tau(x)}x$ will have, under the chaotic hypothesis on $S = S_{\tau(x)}$, an average value $\overline{\tau}$ (x-independent except for a set of data x enclosed in a 0 volume set) and the phase space contraction between two successive timing events will be $\exp -\int_0^{\tau(x)}\sigma(S_tx)dt \equiv (\det\partial S(x)/\partial x)^{-1}$ so that

$$\sigma_+ = \lim_{n\to+\infty} \frac{-1}{n\mathcal{T}} \log\Big(\det \frac{\partial S^n(x)}{\partial x}\Big) = \lim_{n\to+\infty} \frac{-1}{n\mathcal{T}} \sum_{j=1}^{n} \log\det \frac{\partial S}{\partial x}\Big(S^j x\Big) \quad (2.8.5)$$

which will be a constant σ_+ for all points x close to an attracting set for S and outside a set of zero volume. It has to be remarked that the value of the constant is a well known quantity in the theory of dynamical systems being equal to

$$\sigma_+ = \frac{1}{\mathcal{T}} \sum_i \lambda_i \quad (2.8.6)$$

with λ_i being the SRB Lyapunov exponents of S on the attracting set for S.[14]

In the nonequilibrium models considered in Sect. 2.2 the value of $\sigma(x)$ differs from $\varepsilon(x) = \sum_{j>0} Q_j/k_B T_j$ by a time derivative so that, at least under the chaotic hypothesis, the *average phase space contraction equals the entropy production rate of a stationary state*, and $\sigma_+ \equiv \varepsilon_+$.

An important remark is that $\sigma_+ \geq 0$, [27], if the thermostats are efficient in the sense that motions remain confined in phase space, see Sect. 2.1: the intuition is that it is so because $\sigma_+ < 0$ would mean that any volume in phase space will grow larger and larger with time, thus revealing that the thermostats are not efficient ("it is not possible to inflate a balloon inside a (small enough) safe").

Furthermore if $\sigma_+ = 0$ it can be shown, quite generally, that the phase space contraction is the time derivative of an observable, [27, 28] and, by choosing conveniently the measures of the volume elements, a probability distribution will be obtained which admits a density over phase space and which is invariant under time evolution.

A special case is if it is even $\sigma(x) \equiv 0$: in this case the normalized volume measure is an invariant distribution.

A more interesting example is the distribution Eq. (2.8.2) when $T_j \equiv T_i \stackrel{def}{=} T$ and $\mathbf{E} = \mathbf{0}$. It is a distribution which, for the particles in C_0, is a Gibbs distribution with special boundary conditions

$$\mu_0(dx) = e^{-\beta\Big(K_0+U_0+\sum_{j=1}^n \big(U_j+W_j(\mathbf{X}_0,\mathbf{X}_j)\big)\Big)} \prod_{j=1}^{n} \delta(K_j, T) \prod_{j=0}^{n} d\mathbf{X}_j d\dot{\mathbf{X}}_j \quad (2.8.7)$$

and therefore it provides an appropriate distribution for an equilibrium state, [6] and [2, 8]. The more so because of the following consistency check, [6]:

Theorem *If N_i is the number of particles in the i-th thermostat and its temperature is $k_B T_i = \beta^{-1}(1 - 1/3N_i)$ then the distribution in* Eq. 2.8.7 *is stationary.*

[14] The Lyapunov exponents are associated with invariant probability distributions and therefore it is necessary to specify that here the exponents considered are the ones associated with the SRB distribution.

To check: notice that a volume element $dx = \prod_{j=0}^{n} d\mathbf{X}_j d\dot{\mathbf{X}}_j$ is reached at time t by a volume element that at time $t - dt$ had size $e^{\sigma(\mathbf{X},\dot{\mathbf{X}})dt} dx$ and had total energy $H(\mathbf{X} - \dot{\mathbf{X}}dt) = H(\mathbf{X}, \dot{\mathbf{X}}) - dH$. Then compute $-\beta dH + \sigma dt$ via the equations of motion in Fig. (2.2) with the isokinetic constraints Eq. 2.2.3 for $k_B T_i = \beta^{-1}(1 - 1/3N_i)$ obtaining $-\beta dH + \sigma dt \equiv 0$, i.e. proving the stationarity of Eq. 2.8.7.

This remarkable result suggests to *define* stationary nonequilibria as invariant probability distributions for which $\sigma_+ > 0$ and to extend the notion of equilibrium states as invariant probability distributions for which $\sigma_+ = 0$. In this way *a state is in stationary nonequilibrium if the entropy production rate* $\sigma_+ > 0$.

It should be remarked that (in systems satisfying the chaotic hypothesis), as a consequence, the SRB probability distributions for nonequilibrium states are concentrated on *attractors*, defined as subsets $\mathcal{B}$ of the attracting sets $\mathcal{A}$ which have full phase space volume, i.e. full area on the surface $\mathcal{A}$, and minimal fractal dimension, although the closure of $\mathcal{B}$ is the whole $\mathcal{A}$ (which in any event, *under the chaotic hypothesis* is a smooth surface).[15]

In systems out of equilibrium it is convenient to introduce the *dimensionless entropy production rate* and *phase space contraction* as $\varepsilon(x)/\varepsilon_+$ and $\sigma(x)/\varepsilon_+$ and, since ε and σ differ by a time derivative of some function $D(x)$, the finite time averages

$$p = \frac{1}{\tau}\int_0^\tau \frac{\varepsilon(S_t x)}{\varepsilon_+}\,dt \qquad \text{and} \quad p' = \frac{1}{\tau}\int_0^\tau \frac{\sigma(S_t x)}{\sigma_+}\,dt \tag{2.8.8}$$

will differ by $D(S_\tau x) - D(x)/\tau$ which will tend to 0 as $\tau \to \infty$ (in Anosov systems or under the chaotic hypothesis). Therefore for large τ the statistics of p and p' in the stationary state will be close, at least if the function D is bounded (as in Anosov systems).

2.9 Phase Space Contraction in Timed Observations

In the case of discrete time systems (not necessarily arising from timed observations of a continuous time evolution) the phase space contraction (per timing interval) can be naturally defined as

$$\sigma_+ = \lim_{n\to+\infty} -\frac{1}{n}\sum_{j=1}^{n} \log|\det \frac{\partial S}{\partial x}(S^j x)| \tag{2.9.1}$$

as suggested by Eq. (2.8.5).

[15] An attracting set $\mathcal{A}$ is a closed set such that all data x close enough to $\mathcal{A}$ evolve so that the distance of $S^n x$ to $\mathcal{A}$ tends to 0 as $n \to \infty$. A set $\mathcal{B} \subset \mathcal{A}$ with full SRB measure is called an *attractor* if it has minimal Hausdorff dimension, [14]. Typically B is in general a fractal set whether or not $\mathcal{A}$ is a smooth manifold.

There are several interesting interaction models in which the pair potential is unbounded above: like models in which the molecules interact via a Lennard-Jones potential. As mentioned in Sect. 1.1 this is a case in which observations timed to suitable events become particularly useful.

In the case of unbounded potentials (and finite thermostats) a convenient timing could be when the minimum distance between pairs of particles reaches, while decreasing, a prefixed small value r_0; the next event will be when all pairs of particles, after separating from each other by more than r_0, come back again with a minimum distance equal to r_0 and decreasing. This defines a timing events surface Ξ in the phase space M.

An alternative Poincaré's section could be the set $\Xi \subset M$ of configurations in which the total potential energy $W = \sum_{j=1}^{n} W_j(\mathbf{X}_0, \mathbf{X}_j)$ becomes larger than a prefixed bound $\overline{W}$ with a derivative $\dot{W} > 0$.

Let $\tau(x)$, $x \in \Xi$ be the time interval from the realization of the event x to the realization of the next one $x' = S_{\tau(x)}x$. The phase space contraction is then $\exp \int_0^{\tau(x)} \sigma(S_t x)dt$, in the sense that the volume element ds_x in the point $x \in \Xi$ where the phase space velocity component orthogonal to Ξ is v_x becomes in the time $\tau(x)$ a volume element around $x' = S_{\tau(x)}x$ with

$$ds_{x'} = \frac{v_x}{v_{x'}}\, e^{-\int_0^{\tau(x)} \sigma(S_t x)dt}\, ds_x \tag{2.9.2}$$

Therefore if, as in several cases and in most simulations of the models in Sect. 2.2:

(1) v_x is bounded above and below away from infinity and zero
(2) $\sigma(x) = \varepsilon(x) + \dot{D}(x)$ with $D(x)$ *bounded on* Ξ (but possibly unbounded on the full phase space M)
(3) $\tau(x)$ is bounded and (for x outside a zero volume set) has average $\overline{\tau} > 0$

setting $\widetilde{\varepsilon}(x) = \int_0^{\tau(x)} \varepsilon(S_t x)dt$ it follows that the entropy production rate and the phase space contraction have the same average $\varepsilon_+ = \sigma_+$ and likewise

$$p = \frac{1}{m}\sum_{k=0}^{m-1} \frac{\widetilde{\varepsilon}(S^k x)}{\widetilde{\varepsilon}_+} \qquad \text{and} \quad p' = \frac{1}{m}\sum_{k=0}^{m-1} \frac{\widetilde{\sigma}(S^k x)}{\widetilde{\sigma}_+} \tag{2.9.3}$$

will differ by $1/m\big(D\big(S^m x\big) - D(x) + \log v_{S^m x} - \log v_x\big) \xrightarrow[m\to\infty]{} 0$.

This shows that in cases in which $D(x)$ is unbounded in phase space but there is a timing section Ξ on which it is bounded and which has the properties (1)–(3) above it is more reasonable to suppose the chaotic hypothesis for the evolution S timed on Ξ rather than trying to extend the chaotic hypothesis to evolutions in continuous time for the evolution S_t on the full phase space.

2.10 Conclusions

Nonequilibrium systems like the ones modeled in Sect. 2.2 undergo, in general, motions which are empirically chaotic at the microscopic level. The chaotic hypothesis means that we may as well assume that the chaos is maximal, i.e. it arises because the (timed) evolution has the Anosov property.

The evolution is studied through timing events and is therefore described by a map S on a "Poincaré's section" Ξ in the phase space M.

It is well known that in systems with few degrees of freedom the attracting sets are in general fractal sets: the chaotic hypothesis implies that instead one can neglect the fractality (at least if the number of degrees of freedom is not very small) and consider the attracting sets as smooth surfaces on which motion is strongly chaotic in the sense of Anosov.

The hypothesis implies (therefore) that the statistical properties of the stationary states are those exhibited by motions;

(1) That follow initial data randomly chosen with a distribution with density over phase space
(2) Strongly chaotic as in the chaotic hypothesis

and the stationary states of the system are described by the SRB distributions μ which are uniquely associated with each attracting set.

Systems in equilibrium (which in our models means that neither nonconservative forces nor thermostats act) satisfying the chaotic hypothesis can have no attracting set other than the whole phase space, which generically is the energy surface,[16] and have as unique SRB distribution the Liouville distribution, i.e. the chaotic hypothesis implies for such systems that the equilibrium states are described by microcanonical distributions. This means that nonequilibrium statistical mechanics based on the chaotic hypothesis cannot enter into conflict with the equilibrium statistical mechanics based on the ergodic hypothesis.

The main difficulty of a theory of nonequilibrium is that whatever model is considered, e.g. any of the models in Sect. 2.2, there will be dissipation which manifests itself through the non vanishing divergence of the equations of motion: this means that volume is not conserved no matter which metric we use for it, unless the time average σ_+ of the phase space contraction vanishes. Introduction of non Newtonian forces can only be avoided by considering infinite thermostats.

Since the average σ_+ cannot be negative in stationary nonequilibrium systems its positivity is identified with the signature of a genuine nonequilibrium, while the cases in which $\sigma_+ = 0$ are equilibrium systems, possibly "in disguise". If $\sigma_+ > 0$ there cannot be any stationary distribution which has a density on phase space: the stationary states give probability 1 to a set of configurations which have 0 volume in phase space (yet they may be dense in phase space, and often are such, if σ_+ is small).

[16] Excluding, for instance, specially symmetric cases, like spherical containers with elastic boundary.

Therefore any stationary distribution describing a nonequlibrium state cannot be described by a suitable density on phase space or on the attracting set, thus obliging us to develop methods to study such singular distributions.

If the chaotic hypothesis is found too strong, one has to rethink the foundations: the approach that Boltzmann used in his discretized view of space and time, started in [29, p. 5] and developed in detail in [30, p. 42], could be a guide.

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