# Nonequilibrium stationary states and entropy

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In transformations between nonequilibrium stationary states, entropy might not be a well defined concept. It might be analogous to the ''heat content'' in transformations in equilibrium which is not well defined either, if they are not isochoric (i.e., do involve mechanical work). Hence we conjecture that in a nonequilibrium stationary state the entropy is just a quantity that can be transferred or created, such as heat in equilibrium, but has no physical meaning as ''entropy content'' as a property of the system.

## I. THERMOSTATS AND CHAOTIC HYPOTHESIS

In studying equilibrium and nonequilibrium thermodynamics the notion of *thermostat* plays an important role: it is usually defined phenomenologically [1] as a system capable only of exchanging heat without changing its temperature or performing work (hence it is ideally an infinite system).

In a statistical mechanical approach to a theory of the nonequilibrium stationary states of a system which is subject to external nonconservative forces, which (therefore) perform work, thermostats must then be present to avoid that the work performed by the external forces causes an increase of the energy beyond bounds. In statistical approaches the thermostats must be defined as mechanical forces: the routes that one can follow are the following.

(i) Introduce stochastic forces acting on the system (usually on the boundary).

(ii) Assume that the system interacts via conservative forces with infinite systems (''thermostats'') which are initially in equilibrium and which one would like to show that by interacting with the system the thermostats will undergo only changes localized in the vicinity of the contact surfaces.

(iii) Assume that the interaction with the ''outside world'' is modeled by an effective force on the system which balances the work of the external forces working on the system [cf. Eq. (1) below] thus allowing the system to reach stationarity.

The third possibility has recently emerged as a very convenient way of studying the problem, since it at least avoids the virtually untractable theory of the behavior of systems in contact with infinite reservoirs. However it is often regarded as ''unphysical'' because it ''amounts to modifying the system's equations of motion.'' But the equations of motion are modified also if one uses the option (i), while the option (ii) is interesting but not really suitable for investigations which, at least until now, mostly rely on numerical experiments. Furthermore, theoretically the only ''infinite thermostats'' which have been considered are infinite systems of free par-

ticles interacting only with the particles of the system and not directly with each other, a rather restricted case.

Here we shall model thermostats by mechanical forces acting on the system; however, we do not want to make very specific choices of the forces and the thermostats since we are interested only in general properties which would be shared by ''any'' (reasonable) choices of the forces and thermostat models. We think that the mechanical models of thermostats fall into ''equivalence classes,'' just as one thinks that phenomenological thermostats do. Therefore we consider mechanical systems which, in spite of being acted upon by nonconservative forces, are kept in a nonequilibrium stationary state with the help of other mechanical (thermostatic) forces, and study which relations, if any, can be established about transitions between stationary states [2]. We restrict ourselves here to transformations between stationary states which are *quasistatic* transformations through intermediate stationary states. This means that on the time scale of the observations the control parameters (e.g., volume, strength of the external forces, etc.) of the stationary states are kept fixed long enough so that the system can at any time can be considered to be in a stationary state. This is a generalization of reversible transitions in equilibrium.

We consider only systems consisting of many particles and we do *not* consider systems that are modeled by continua. Continua could be considered but one must first understand the thermodynamics of simple systems [3]. The particle motions occurring in a simple system are assumed to be chaotic. The *chaotic hypothesis* [4], essentially states that an isolated system of particles has a chaotic evolution on microscopic time scales (see below).

A simple system will be described by a differential equation in its phase space: we write it as $\dot{x} = X_E(x)$ where $x = (\dot{\mathbf{q}}, \mathbf{q}) \in \mathbb{R}^{6N} \equiv \Omega$ (*phase space*), $N$ = number of particles, $m$ = mass of the particles, with

$$m\ddot{\mathbf{q}} = \mathbf{f}(\mathbf{q}) + \mathbf{E} \cdot \mathbf{g}(\mathbf{q}) - \boldsymbol{\vartheta}_E(\dot{\mathbf{q}}, \mathbf{q}) \equiv \mathbf{X}_E(x), \qquad (1)$$

where $\mathbf{f}(\mathbf{q})$ describes the internal (conservative) forces (e.g., hard cores), $\mathbf{E} \cdot \mathbf{g}(\mathbf{q})$ represents the ''active external forces'' (nonconservative for the reasons mentioned at the beginning) acting on the system. For definiteness we suppose that they are locally conservative (like an electromotive force) but not globally, and $\boldsymbol{\vartheta}_E$ is the force law which models the action

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exerted by the thermostat on the system to keep it from indefinitely acquiring energy: this is why we shall call it a *mechanical thermostat*. Linearity of the dependence on the "fields" **E** is only for convenience: we are *not* assuming them to be small (the theory of linear nonequilibrium is amply discussed in the literature [5]). More generally the external forces could be velocity dependent and even time dependent (periodically) but we restrict ourselves to positional forces only for simplicity.

Models of thermostats in the above sense can be very different even for the same macroscopic system; for instance (a list far from exhaustive), (1) assuming the system to have hard cores (e.g., a granular material of the type considered in Ref. [6]) one can consider inelastic collisions, e.g., suppose that the head-on component of the energy is decreased by a scale factor $\eta < 1$ upon each collision or, *alternatively*, the total energy of the two colliding particles is rescaled after a collision and assigned a value $2 \frac{3}{2} k_B T$ (this is essentially "Drude's conduction model") [7]; or (2) assuming that there is a background friction $\vartheta_i = -\nu \dot{q}_i$, $\nu > 0$, for all components of $\ddot{x}_j$; or (3) assuming *minimum effort* to keep, say, the total kinetic energy or the total energy constant ("*Gaussian thermostat*" [8]).

*Remark.* The restriction that the external forces $\mathbf{E} \cdot \mathbf{g}(\mathbf{q})$ be positional is a strong restriction as it does not allow velocity dependent forces or several different thermostats as needed in any heat conduction problem where the nonequilibrium stationary state is achieved by putting the system in contact with two reservoirs without any external forces acting. However, such cases could also be considered [9], but we do not treat them here since we want to restrict ourselves to the simplest case.

We shall assume about the system which we consider the *chaotic hypothesis* [4] [The system evolution is supposed to be as chaotic as possible, i.e., to be hyperbolic (one also says, technically, that the system is "an Anosov system").], which will be a key assumption in our analysis.

## II. SRB STATISTICS AND NONEQUILIBRIUM ENSEMBLES

Any initial state $x$, randomly chosen in phase space with a probability distribution which has a density in phase space [i.e., such that the probability of a phase point $\dot{\mathbf{q}}, \mathbf{q}$ to be in $d\dot{\mathbf{q}} d\mathbf{q}$ has the form $\rho(\dot{\mathbf{q}}, \mathbf{q}) d\dot{\mathbf{q}} d\mathbf{q}$ for some probability density $\rho(\dot{\mathbf{q}}, \mathbf{q}) \geq 0$ in phase space] *will admit a statistics* (under the above chaotic assumption): i.e., for all (smooth) observables $F$,

$$\lim_{T \to \infty} \frac{1}{T} \int_0^T F(S_t x) dt = \int_\Omega \mu_{\mathbf{E}}(dy) F(y), \qquad (2)$$

where $\mu_{\mathbf{E}}$ is a stationary probability distribution on phase space, called the *SRB distribution* or also *SRB statistics* [3,10–12]. This is a (nontrivial) consequence of the above chaotic hypothesis.

*Definition.* A system in a microscopic state $x$, which has SRB statistics $\mu_{\mathbf{E}}$, is said to be in the stationary state $\mu_{\mathbf{E}}$.

The collection of all stationary states of a system that are constructed by varying the parameters (typically the volume $V$ of the container, the number of particles $N$, the external forces **E**, etc.) will be called a "nonequilibrium Ensemble."

The *Ensemble* (with capital $E$) is therefore a collection of probability distributions which we distinguish from what, following Gibbs, has become established terminology where *ensemble* indicates *a single element* of the collection, with fixed control parameters: what is usually called simply the "microcanonical ensemble with parameters $U, V$" is here just a single element of the collection (i.e., the Ensemble) of microcanonical probability distributions.

The notion of Ensemble in nonequilibrium is wider than in equilibrium since it depends *also* on the equations of motion, because of the presence there of the thermostats. However, one expects that, as happens in equilibrium statistical mechanics, there should be "equivalent Ensembles" corresponding to classes of different possible models for thermostats acting on a system [3,11].

Equilibrium is a special case of a nonequilibrium stationary state: in such case $\mathbf{E} = \mathbf{0}$ and $\vartheta_{\mathbf{E}} = \mathbf{0}$ and the chaotic hypothesis implies the validity of the ergodic hypothesis [11]; the Ensemble (or collection) of SRB distributions each of which can be parametrized by the total energy $U$ and volume $V$ coincides with the corresponding collection of microcanonical ensembles [11]. Furthermore, in general, the chaotic hypothesis implies that observables that are represented by smooth functions on phase space have finite time correlations which converge exponentially fast to their stationary state averages (i.e., SRB averages).

We now want to consider which relations can be established in general between the properties of stationary states that can be transformed into one another by changing reversibly the external parameters, just as is done on equilibrium states.

In fact, if we limit ourselves to equilibrium states first then it is well known, since Boltzmann (in his papers in the period 1866–1884, see Ref. [13]), that if a transformation generates an energy variation $dU$ and a volume variation $dV$ when the pressure (defined as a time average of a function defined on phase space, see for instance Ref. [11]) is $p$ and the average kinetic energy is $\frac{3}{2} N k_B T$ then, see Ref. [11] appendixes A1.1 and A9.3,

$$\frac{dU + p \, dV}{T} = (\text{exact differential}), \qquad (3)$$

while $dU + p \, dV$ is not exact, *except* in the isochoric case (i.e., when $dV = 0$) and it is called the *heat transferred* from the heat reservoirs to the system. It makes no sense to talk of *heat content* contained in the system [14], unless one limits oneself to isochoric transformations: there is no heat content of a system because one cannot distinguish between the heat and the mechanical work contents unless one allows only isochoric transformations in which the system performs no work (and in that case it is just another name for the internal energy).

Defining the *entropy* content of a system as an integral $S$ of the exact differential $(dU+pdV)/T$, an immediate question is whether one can extend the notion of entropy content to nonequilibrium states.

## III. ENTROPY PRODUCTION RATE AND TEMPERATURE

The proposal that emerges from various theoretical considerations and a number of numerical experiments [8,11,15,16], is to define, if $k_B$ is Boltzmann's constant,

*Definition.* The entropy production rate in a stationary state $\mu_{\mathbf{E}}$ is $k_B\sigma_+$ with [cf. Eq. (2)]:

$$\sigma_+ \overset{def}{=} \langle\sigma\rangle = \int_\Omega \mu_{\mathbf{E}}(dx)\sigma(x), \qquad (4)$$

where $\sigma(x) = -$ divergence of $\mathbf{X}_{\mathbf{E}}(x)$ [i.e., $\sigma(x)$ is the phase space contraction rate] and $\mu_{\mathbf{E}}$ is the SRB statistics.

This definition elicits a few comments.

(a) There is no generally accepted definition of entropy in nonequilibrium stationary states.

(b) In several thermostat models considered in the literature the average divergence $\sigma_+$ of the equations of motion is essentially related to $W$, the average work per unit time done by the thermostating forces, i.e., to the time average $W$ of $\dot{\mathbf{q}}\cdot\boldsymbol{\vartheta}(\mathbf{q},\dot{\mathbf{q}})$, which in stationary states equals the average work done by the external forces. For instance if $\boldsymbol{\vartheta}(\mathbf{q},\dot{\mathbf{q}})$ is proportional to $\dot{\mathbf{q}}$, i.e., $\boldsymbol{\vartheta}(\mathbf{q},\dot{\mathbf{q}}) = \alpha(\dot{\mathbf{q}},\mathbf{q})\dot{\mathbf{q}}$ for some function $\alpha$, then $W = \langle\alpha\dot{\mathbf{q}}^2\rangle$ while $\sigma_+ = \langle\sigma\rangle = 3N\langle\alpha\rangle + \langle(\partial_{\dot{\mathbf{q}}}\alpha)\cdot\dot{\mathbf{q}}\rangle$: hence $W \simeq \langle\alpha\rangle 2K$ and $\sigma_+ \simeq 3N\langle\alpha\rangle$ so that in such cases $W$ and $\sigma_+$ are related by $\sigma_+ = W/2K/3N$. Since the work done by the thermostating forces is naturally interpreted as the heat that the system cedes to the thermostat we see that in the cases considered [i.e., $\boldsymbol{\vartheta}(\mathbf{q},\dot{\mathbf{q}}) = \alpha(\dot{\mathbf{q}},\mathbf{q})\dot{\mathbf{q}}$] the quantity $\sigma_+$ has the meaning of the entropy increase of the thermostat.

(c) An important general theorem [17], guarantees that $\sigma_+ \geq 0$, and $\sigma_+ = 0$ corresponds to the case in which the SRB distribution $\mu_{\mathbf{E}}$ admits a density on phase space, a case that one naturally identifies with an equilibrium state and which essentially happens only if $\mathbf{E}=\mathbf{0}$.

Certainly the above three properties are, at best, only an indication that the phase space contraction can be interpreted as the entropy increase of the thermostats (in the classical sense of the word and due to the heat generated by the system). If we used phenomenological thermostats they would be systems in thermal equilibrium and at a fixed temperature so that the heat absorbed per unit time would generate an entropy increase of the thermostats which is well defined. Here one has to bear in mind that the notion of heat absorbed by a mechanical thermostat as well as the notion of its temperature are *new concepts*. We use the arbitrariness offered us by the lack of a generally accepted definition of these concepts to conjecture the above definition of the entropy production rate on the basis of the general result in (c) which guarantees the positivity that is desired for compatibility with classical thermodynamics.

The notion of temperature of a thermostat is however still missing but the above definition leads to a definition of an effective temperature of the thermostating forces (we stress that there is no universally accepted definition of temperature in systems out of equilibrium, even if stationary [2,6]). Here we propose the following.

*Definition.* The (effective) temperature $T$ of the thermostats for a stationary nonequilibrium state is

$$T = \frac{W}{k_B\sigma_+}, \qquad (5)$$

where $W$ is the average work per unit time done on the system by the external forces, equal to the average work $\dot{Q}$ done on the thermostating forces, and $k_B\sigma_+$ is the entropy production rate.

The equality between $W = \langle\mathbf{E}\cdot\mathbf{g}(\mathbf{q})\cdot\dot{\mathbf{q}}\rangle$ and $\dot{Q} = \langle\boldsymbol{\vartheta}\cdot\dot{\mathbf{q}}\rangle$ is due to the fact that the internal forces being conservative perform zero work on the average.

*Remark.* The situations in which there is heat conduction between different thermostats is not considered here. In such cases one has at least two thermostats acting on the system: i.e., the thermostating force $\boldsymbol{\vartheta}$ is then the sum of, for instance, forces $\boldsymbol{\vartheta} = \boldsymbol{\vartheta}_1 + \boldsymbol{\vartheta}_2$, which perform the work $-\dot{Q}_1$ and $-\dot{Q}_2$, respectively, so that the divergence $\sigma(x)$ is the sum of two quantities $\sigma_1(x)$ and $\sigma_2(x)$. Therefore in such cases it will be natural to define the temperatures of the two thermostats as $T_i = \dot{Q}_i/k_B\sigma_{i+}$ we do not discuss the matter further since, from the outset, we are not considering situations in which the system is subject to several thermostating forces.

The above definition does not make sense as such in equilibrium because it becomes 0/0: however, one can imagine introducing a small forcing $\mathbf{E}$ and a corresponding thermostat. Then in the limit of vanishing, forcing this yields a definition of $T$ which by the "fluctuation dissipation theorem" can be checked to be the correct equilibrium temperature [9,18–20].

Our definition of nonequilibrium temperature has already been hinted at by Bonetto and Menon as well as used in the literature [6,18], in particular cases.

Adopting the above concepts leads naturally to giving up the possibility of defining the entropy content of a nonequilibrium stationary state because the system creates entropy at a constant rate and if one would insist in defining the entropy content of a dissipating (i.e., with $\sigma_+>0$) stationary state one would be compelled to assign to it a value $-\infty$. Thus in our view of nonequilibrium stationary states the entropy ends up to be undefined and one can speak meaningfully only of "entropy production" or "entropy transfer," much as the "heat content" of a system is undefined in equilibrium, but production and transfer of heat are well defined.

The divergence of the entropy has been discussed in Ref. [11] (see Chap. 9.7) and Refs. [2,21]. Other approaches which try to define entropy as a finite quantity are in Refs. [22–24].

## IV. DISCUSSION

(1) Having defined the notion of entropy production rate one can define a "duality" between fluxes $J_j$ and forces $E_j$

using $k_B \sigma_+ = k_B \int \mu(dx) \sigma(x)$ as a "generating function:"

$$J_j(\mathbf{E}) = k_B \frac{\partial \sigma_+}{\partial E_j},$$

which, in the limit $\mathbf{E} = \mathbf{0}$, leads to Onsager's reciprocity and to Green–Kubo's formulas for transport [19,20].

(2) We have proposed a general definition of entropy production rate and of temperature for a class of stationary states. But a new definition is really useful if it is associated with new results: we think that such new results may already be around and cluster around the *fluctuation theorem*, for which we refer to the literature [2,4,6,25–29].

(3) The reason for our conjecture on the absence of an entropy content in nonequilibrium stationary states differs from the absence of heat content in equilibrium. This is because in equilibrium the heat content cannot be defined separately from the mechanical energy content [14]. However in a nonequilibrium stationary state the impossibility to define entropy content is due to the steady entropy production, which makes the entropy content $-\infty$. In spite of that there is an analogy in that both quantities can be transferred or produced and they can even be defined if one limits oneself to consider a suitably restricted class of transformations (e.g., isochoric transformations between equilibrium states for what concerns heat or general transformations between equilibrium states for what concerns entropy).

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