WHAT PHYSICAL QUANTITIES MAKE SENSE IN NONEQUILIBRIUM STATISTICAL MECHANICS?

by David Ruelle*.

Abstract. Statistical mechanics away from equilibrium is in a formative stage, where general concepts slowly emerge. We restrict ourselves here to the study of transport phenomena, especially heat transport, and consider several well-studied classes of systems: finite systems with isokinetic thermostats, infinite classical Hamiltonian systems, infinite quantum spin systems. For those classes we discuss how various physical quantities can be defined. Our review however leaves several basic questions quite open.

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1 Introduction.

Statistical mechanics, as seen by Boltzmann, is an attempt to understand the bulk properties of matter in terms of the dynamics of its microscopic constituents. The bulk properties of matter are described at the macroscopic level by thermodynamics.

1.1 Thermodynamics: equilibrium and nonequilibrium.

Equilibrium thermodynamics is based on the observation that some states of matter, the equilibrium states, are operationally definable. One can associate with equilibrium states some quantities, notably temperature and entropy, that are not part of macroscopic mechanics. In equilibrium "nothing happens" at the macroscopic level. In nonequilibrium thermodynamics "things happen": heat is transferred, temperature may depend on spatial coordinate and on time. More importantly, the global entropy is not constant in time, it always increases. There is a great variety of nonequilibrium phenomena, including chemical reactions, and the so-called transport phenomena. We shall be especially interested in these transport phenomena, where a gradient of temperature (or concentration, or velocity in a fluid) produces a "transport" or flux of heat (or solute, or momentum). A quantity of particular interest is the entropy production rate (entropy produced per unit time per unit volume).

1.2 Equilibrium statistical mechanics.

Maxwell, Boltzmann and Gibbs have understood that the equilibrium states of thermodynamics have a probabilistic description at the microscopic level. If $H(\mathbf{p},\mathbf{q})$ is the Hamiltonian depending on the momentum variables $\mathbf{p} = (p_1,\ldots,p_N)$ and configuration coordinates $\mathbf{q} = (q_1,\ldots,q_N)$, the probability that $\mathbf{p},\mathbf{q}$ are microscopically realized is given by the "normalized Boltzmann factor"

$$P(\mathbf{p},\mathbf{q})\,d\mathbf{p}\,d\mathbf{q} = \frac{1}{Q}\exp[-\frac{1}{kT}H(\mathbf{p},\mathbf{q})]\,d\mathbf{p}\,d\mathbf{q}$$

where T is the absolute temperature, and k is Boltzmann's constant. We shall use the "inverse temperature" $\beta = 1/kT$ and take $k = 1$. The above probability distribution is known as the "canonical ensemble", and one shows that is is in some sense equivalent to other "ensembles" in the limit of a large system (thermodynamic limit). We shall not go into details, but note that equilibrium statistical mechanics is an *emergent theory* with respect to Hamiltonian mechanics: it applies only to certain systems (like particles with short range interactions), certain states (equilibrium states), and introduces the new concept of absolute temperature. The concept of entropy can also be defined, it is given by

$$-\int P(\mathbf{p},\mathbf{q})\,d\mathbf{p}\,d\mathbf{q}\log P(\mathbf{p},\mathbf{q})$$

(it is basically the logarithm of the volume of occupied phase space, *i.e.*, the part of $(\mathbf{p},\mathbf{q})$-space where the probability of the system is somehow significant). A fundamental feature of the emergent theory of equilibrium statistical mechanics is that it ignores dynamics: time does not occur. Of course, if one tries to justify the ensembles of equilibrium statistical mechanics one will have to use dynamics, but once one has the ensembles, the theory proceeds without dynamics. Equilibrium statistical mechanics is conceptually simple, it has been an enormously successful physical theory, and has also led to beautiful mathematical developments.

1.3 Nonequilibrium statistical mechanics close to equilibrium.

While Boltzmann is one of the fathers of equilibrium statistical mechanics, he is *the* father of nonequilibrium statistical mechanics. He has basically explained why entropy increases in nonequilibrium (see [14]). Here is the idea: Hamiltonian dynamics preserves phase space volume (Liouville's theorem) but different regions of phase space may be so finely mixed by the dynamics that they progressively become indistinguishable. The apparent entropy, which corresponds to the mixed volume is thus larger than the entropy corresponding to the volume of an initial region.

Nonequilibrium statistical mechanics is now relatively well understood close to equilibrium. This development, which took place around the middle of the 20th century, is linked to the names of Onsager, Green, Kubo, ...(see [4]). A great simplification that occurs close to equilibrium is that thermostats are not needed, and one can obtain transport coefficients by some kind of first order perturbation theory around equilibrium (linear response theory). It turns out that the transport coefficients (*i.e.*, diffusion coefficients, viscosity, ...) are given in terms of the well understood equilibrium states, and the microscopic dynamics in these states, *i.e.*, time correlation functions. Dynamics appears thus here, but in a limited way.

Note that chemical reactions are not "close to equilibrium" in the sense needed for the above ideas to apply. Also, the mathematical justification of linear response theory is still unsatisfactory, because the microscopic dynamics in equilibrium states remains poorly understood. In fact, it seems that to make sense of linear response close to equilibrium requires understanding nonequilibrium statistical mechanics away from equilibrium (this is often called "far from equilibrium", but "a finite distance away from equilibrium" is what is really meant).

2 Nonequilibrium statistical mechanics away from equilibrium.

We shall concern ourselves here with transport phenomena and, more specifically, with heat transfer. We want thus to consider systems that are macroscopically described by a temperature field, but no density or velocity field. We have thus one macroscopically conserved quantity (energy, or heat), and no particles for which we would have to consider conservation of particle number and perhaps of momentum. The fact is that the discussion of moving particles entails technical difficulties that we want to avoid. We shall in fact restrict ourselves to three Classes of nonequilibrium systems for which the time evolution is mathematically well controlled. We present now our three Classes.

2.1 Systems with isokinetic thermostatting [8], [11].

These are systems described by $2N$ real variables: $p_1, \ldots, p_N, q_1, \ldots, q_N$, and we write $\mathbf{p} = (p_1, \ldots, p_N)$, $\mathbf{q} = (q_1, \ldots, q_N)$.

Case I

We assume, in the simplest case, that the time evolution is

$$\frac{d}{dt}\begin{pmatrix}\mathbf{p}\\ \mathbf{q}\end{pmatrix}=\begin{pmatrix}\xi(\mathbf{q})-\alpha\mathbf{p}\\ \mathbf{p}/m\end{pmatrix}$$

where $\alpha=\mathbf{p}\cdot\xi(\mathbf{q})/\mathbf{p}^2$. This differs from a Hamiltonian evolution equation by the fact that ξ need not be a gradient (*i.e.*, we need not have $\xi=-\nabla_{\mathbf{q}}U(\mathbf{q})$), and that a term $-\alpha\mathbf{p}$ has been added. We have

$$\frac{d}{dt}\frac{\mathbf{p}^2}{2m}=\frac{1}{m}\mathbf{p}\cdot\frac{d}{dt}\mathbf{p}=0$$

i.e., the kinetic energy does not change.

Note that a probability measure $\rho(\mathbf{x})\,d\mathbf{x}$ has a (Gibbs) entropy

$$S=-\int\rho(\mathbf{x})d\mathbf{x}\,\log\rho(\mathbf{x})$$

One finds quite generally, for the time evolution given by a vector field X, that

$$\frac{dS}{dt}=\int\rho(\mathbf{x})d\mathbf{x}\,\mathrm{div}X=\int\rho(d\mathbf{x})\,\mathrm{div}X$$

where the div is with respect to $d\mathbf{x}$, and the right-hand side makes sense even if the measure ρ is singular. It is argued that the rate of creation of entropy by the system is $-dS/dt$: this is the entropy that the external world sees coming out of the system, while the entropy of the system tends to $-\infty$, and the measure describing it tends to a singular nonequilibrium steady state (NESS) ρ. The rate of entropy production can thus be identified to the rate of volume contraction in phase space [1]. In our case

$$-\mathrm{div}X=\nabla_{\mathbf{p}}\cdot(\alpha\mathbf{p})=N\alpha+\mathbf{p}\cdot\nabla_{\mathbf{p}}\alpha=(N-1)\alpha$$

We may write $\alpha=w/2K$where $w=\mathbf{p}\cdot\xi(\mathbf{q})/m$ is the work per unit time performed by ξ and $K=\mathbf{p}^2/2m$ is the kinetic energy, which is constant. We may associate with K a temperature β^{-1} such that $K=(N-1)\beta^{-1}/2$ (equipartition of energy suggests a factor N rather than $N-1$, but remember that $\mathbf{p}$ is constrained here to an $N-1$ dimensional manifold). We may thus write

$$-\mathrm{div}X=(N-1)\alpha=\beta w$$

hence

$$\text{rate of entropy creation}=(N-1)\int\alpha=\beta\int w$$

where the integral is taken with respect to the NESS: this is the usual thermodynamic relation.

Case II

Instead of thermostatting all N degrees of freedom to temperature β^{-1} for a system with nongradient force ξ, we may also consider a Hamiltonian system where we fix the kinetic energy of a subsystem X_1 with N_1 degrees of freedom to a value K_1, and the kinetic energy of a subsystem X_2 with N_2 degrees of freedom to a value K_2. This means that we replace in the equation of motion $\xi - \alpha\mathbf{p}$ by $\xi - \alpha_1\mathbf{p}_1 - \alpha_2\mathbf{p}_2$ where we now take $\xi = -\nabla_{\mathbf{q}}U(\mathbf{q})$, $\alpha_1 = \xi\cdot\mathbf{p}_1/\mathbf{p}_1^2$, $\alpha_2 = \xi\cdot\mathbf{p}_2^2$ (we use the notation $\mathbf{p}_1 = (p_i)_{i\in X_1}$ and $\mathbf{p}_2 = (p_i)_{i\in X_2}$). We write $\beta_1 = 2K_1/(N_1-1)$, $\beta_2 = 2K_2/(N_2-1)$ and assume $\beta_1^{-1} < \beta_2^{-1}$. The energy per unit time received by the ith thermostat is $w_i = \mathbf{p}_i\cdot\xi(\mathbf{q})/m$, and

$$-\mathrm{div}X = \nabla_{\mathbf{p}}\cdot(\alpha_1\mathbf{p}_1+\alpha_2\mathbf{p}_2) = N_1\alpha_1 + N_2\alpha_2 + \mathbf{p}_1\cdot\nabla_{\mathbf{p}_1}\alpha_1 + \mathbf{p}_2\cdot\nabla_{\mathbf{p}_2}\alpha_2$$

$$= (N_1-1)\alpha_1 + (N_2-1)\alpha_2 = \beta_1 w_1 + \beta_2 w_2$$

Since the forces inside the system are Hamiltonian, assuming that the energy of the system remains bounded gives $\int w_1 + \int w_2 = 0$, where the integral is with respect to the NESS, hence

$$\text{rate of entropy creation} = (\beta_1 - \beta_2)\int w_1$$

which is the usual thermodynamic relation.

One can argue that, in both Case I and Case II, the average of $-\mathrm{div}X$ in the NESS is ≥ 0 (basically this is because the volume in phase space cannot indefinitely increase), and this gives the correct (positive) sign for $\int w$ or $\int w_1$.

2.2 Infinite systems of classical rotators [18]**.**

Let L be a countable set and Γ a graph with vertex set L. For each $x \in L$ we consider a "rotator" described by variables $q_x \in \mathbf{T}$, $p_x \in \mathbf{R}$ and with hamiltonian $H_x = p_x^2/2m + U_x(q_x)$. We couple these rotators by interaction potentials $W_{\{x,y\}}(q_x, q_y)$ when $\{x, y\} \in \Gamma$. To obtain the Hamiltonian of the system in a finite region Λ we let Γ_Λ be the restriction of Γ to Λ and write

$$H_\Lambda = \sum_{x\in\Lambda} H_x + \sum_{\{x,y\}\in\Gamma_\Lambda} W_{\{x,y\}}(q_x, q_y)$$

We assume that the graph Γ is finite dimensional and that that the U_x, $W_{\{x,y\}}$ and their derivatives are uniformly bounded (we omit here technical details). It is also allowed to introduce an "external" (nongradient) force ξ acting on a finite number of rotators (corresponding to a finite set $\Lambda_0 \subset L$). One can then prove an existence and uniqueness theorem for the time evolution (f^t) of the infinite sysem of oscillators just described.

Let ℓ denote a state, *i.e.*, a probability measure on the infinite dimensional phase space of our system, then the time-evolved state $f^t\ell$ is defined for all t and one can take as nonequilibrium steady states the limits when $T \to \infty$ of

$$\frac{1}{T}\int_0^T dt\, f^t\ell$$

We choose as initial state ℓ a Gibbs state, *i.e.*, a limit of $Z_\Lambda^{-1} e^{-\tilde{H}_\Lambda}$ when the finite set $\Lambda \subset L$ tends to L, with

$$\tilde{H}_\Lambda = \sum_{x \in \Lambda} \left(\frac{p_x^2}{2m} + \tilde{U}_x(q_x)\right) + \sum_{\{x,y\} \in \Gamma_\Lambda} W_{\{x,y\}}(q_x, q_y)$$

and Z_Λ^{-1} a normalization factor. If we take $\tilde{H} = \beta H$ outside of a finite region, our initial state is at temperature β^{-1} (outside of the finite region). Another possibility is to take $L = L_1 \sqcup L_2 \sqcup$ finite region, and arrange that the initial state ℓ is at temperature β_1^{-1} in the infinite set L_1, and at temperature β_2^{-1} in the infinite set L_2. Given a finite set $X \subset L$ the state $f^t \ell$, integrated over the variables p_x, q_x for $x \notin X$ is of the form

$$\ell_X^t(\mathbf{p}_X, \mathbf{q}_X)\, d\mathbf{p}_X\, d\mathbf{q}_X$$

where $\mathbf{p}_X = (p_x)_{x \in X}$, $\mathbf{q}_X = (q_x)_{x \in X}$, and ℓ_X^t is a smooth function bounded by

$$C_1(t) e^{-C_2(t)\mathbf{p}^2}$$

In particular, one can associate with X, t an entropy

$$S^t(X) = -\int d\mathbf{p}_X\, d\mathbf{q}_X\, \ell_X^t(\mathbf{p}_X, \mathbf{q}_X) \log \ell_X^t(\mathbf{p}_X, \mathbf{q}_X)$$

and also a conditional entropy

$$\check{S}^t(X) = \lim_{\Lambda \to \infty} (S^t(\Lambda) - S^t(\Lambda \backslash X))$$

It is then a natural idea to try to define the rate of entropy production in X as the time average of $-dS^t(X)/dt$ or $-d\check{S}^t(X)/dt$, *i.e.*,

$$e(X) = \lim_{T \to \infty} \frac{S^0(X) - S^T(X)}{T} \qquad , \qquad \check{e}(X) = \lim_{T \to \infty} \frac{\check{S}^0(X) - \check{S}^T(X)}{T}$$

(the use of $e(X)$ was proposed by Evans and coworkers [19], see also [9], [15]). We may again consider two cases.

Case I

There is an external force ξ and the system is thermostatted at temperature β^{-1}. Then

$$0 \le e(X) \le \check{e}(X) \le \beta \times \text{energy flux from } \xi$$

Case II

No external force, but two thermostats at temperatures $\beta_1^{-1} < \beta_2^{-1}$. Then

$$0 \le e(X) \le \check{e}(X) \le (\beta_1 - \beta_2) \times \text{energy flux to thermostat 1}$$

2.3 Infinite quantum spin systems.

To each point x of a countably infinite set L, a finite dimensional Hilbert space $\mathcal{H}_x$ is attached. For finite $X \subset L$ we let $\mathcal{A}_X$ be the algebra of bounded operators on $\otimes_{x\in X}\mathcal{H}_x$. With natural identifications, all the $\mathcal{A}_X$ are subalgebras of a C*-algebra $\mathcal{A}$, such that $\cup_{X\text{finite}}\mathcal{A}_X$ is norm-dense in $\mathcal{A}$. Choosing a self-adjoint $\Phi(X) \in \mathcal{A}_X$ for each X, we define a formal Hamiltonian

$$H = \sum_X \Phi(X)$$

Under reasonable assumptions on the $||\Phi(X)||$, Robinson [3] has shown that H defines a time evolution, in the sense of a one-dimensional parameter group of $*$-automorphisms α^t of the algebra $\mathcal{A}$. One writes $L = L_1 \sqcup L_2 \sqcup$finite region and one introduces, as initial state, a state σ on $\mathcal{A}$ (=normalized positive linear form) describing equilibrium at temperature β_1^{-1} in the infinite set L_1 and equilibrium at temperature β_2^{-1} in the infinite set L_2. By a compactness argument, one can let T tend to $+\infty$ in such a way that the limits

$$\lim \frac{1}{T}\int_0^T dt\, \sigma(\alpha^t A) = \rho(A)$$

exist, defining a nonequilibrium steady state ρ. It can be proved [16],[12] that the thermodynamic expression for the entropy production is nonnegative:

$$(\beta_1 - \beta_2) \times \text{energy flux to thermostat } 1 \geq 0$$

3 A study of physical quantities.

We have considered three Classes of systems which may describe nonequilibrium: (1) finite systems with IK thermostatting, (2) infinite systems of classical rotators, (3) infinite quantum spin systems. For Classes (1), (2) we could have an external force + thermostat (Case I). For Classes (1)-(3) we could have two thermostats at different temperatures (Case II). We shall now discuss which physical quantities can be associated with different types of systems.

In all the cases considered, the time evolution ((f^t) for (1),(2), (α^t) for (3)) is well defined. For the Class (1), the IK thermostatting is part of the equations of motion, and we can take a somewhat arbitrary initial condition $\ell(\mathbf{p},\mathbf{q})\,d\mathbf{p}\,d\mathbf{q}$ with ℓ continuous decreasing fast as $\mathbf{p} \to \infty$. For Classes (2),(3), the thermostatting is part of the initial condition ℓ or σ. By compactness, we may choose $T \to \infty$ so that these time averages tend (in a weak sense) to a state ρ. This state is invariant under time evolution and we call ρ a nonequilibrium steady state (NESS). Note that for Class (1) (IK thermostatting), the NESS ρ is expected to be a singular measure, this is because we want nontrivial entropy production

$$e = \lim_{T\to\infty} \frac{S^0 - S^T}{T} > 0$$

This implies $S^T \to -\infty$, hence $f^T\ell \to$ singular. Note however, that if $X \subset \{1,\ldots,N\}$ is sufficiently small, the projection ρ_X of the NESS to X might be absolutely continuous. Similarly, for Class (2) systems, the ρ_X for finite X may be absolutely continuous.

3.1 Temperature.

A priori, the temperature of the thermostats is well defined. For infinite thermostats (Classes (2),(3)) this should be physically the temperature far inside the thermostats. But note that we must require that the thermostats have dimension ≥ 3. Indeed, if we consider a macroscopic continuous description of our system, it would have a temperature distribution satisfying the heat equation, and an asymptotically constant value of the temperature at infinity is not possible in dimensions 1 and 2.

For systems locally close to equilibrium, one could define a local temperature, but in general a local temperature would not seem to make much physical sense, because the local velocity distribution cannot be expected to be Maxwellian.

One might want to conjecture that, for a system with two thermostats at temperatures $\beta_1^{-1} < \beta_2^{-1}$, any reasonably defined local temperature $\tilde{\beta}^{-1}$ would satisfy $\beta_1 > \tilde{\beta} > \beta_2$. Let me argue that this is incorrect. Indeed, we may imagine that our system contains a little green man (or woman) who, seeing a warm and a cold source, uses them to power an engine, and then either warms or cools some part of the system outside of the range $[\beta_1^{-1}, \beta_2^{-1}]$. In view of this remark we require, for Class (2) systems, that for each finite X the energy of the subsystem X is bounded independently of time. Note that this requirement could be violated in Case I if the thermostat had dimension < 3, because the energy produced by the external force could not be evacuated at the rate at which it is produced.

3.2 Entropy.

The total entropy is expected to diverge for an infinite system. We shall thus try to give a meaning to the entropy of a finite set X in the NESS ρ. We shall discuss the Gibbs entropy $S_\rho(X)$ because other definitions of entropy require a system close in some sense to equilibrium (see [14]). For Class (1) systems (IK thermostatted), we expect the NESS ρ to be singular, hence $S_\rho(\{1,\ldots,N\}) = -\infty$. Of course if ρ is an equilibrium state $S_\rho(\{1,\ldots,N\})$ is finite, and one can try to extend the definition away from the equilibrium states [17], but this can be done consistently only close to equilibrium. For sufficiently small $X \subset \{1,\ldots,N\}$, it appears possible that $S_\rho(X)$ is finite. For Class (2) systems, it is believable that the projection ρ_X of the NESS to the finite region X is absolutely continuous and with finite entropy (see [5],[6],[2]), at least if X is disjoint from the region where an external force ξ is acting (Case I). For Class (3) systems (quantum spins), the von Neumann entropy $S_\rho(X) = -\mathrm{tr}\rho_X \log \rho_X$ is always finite. It would remain to discuss the possible use and physical meaning of $S_\rho(X)$ when this quantity is finite.

3.3 Global entropy production.

There is a thermodynamic formula for the global entropy production rate e. In Case I we have

$$e = \beta \times \text{energy flux from } \xi$$

In Case II

$$e = (\beta_1 - \beta_2) \times \text{energy flux to thermostat 1}$$

and one has $e \geq 0$. This result, to be proved for each Class of systems considered, is non trivial, it means that the energy flows in the "right" direction.

For systems with an IK thermostat we can also express the rate of entropy production in terms of phase space volume contraction, and this has led to the important fluctuation theorems [7], [10].

3.4 Local entropy production.

For infinite classical Hamiltonian systems (our Class (2)) Evans and coworkers [19] have proposed to define the rate of entropy production in a finite region X as the time average of $-dS^t(X)/dt$, *i.e.*,

$$e(X) = \lim_{T\to\infty} \frac{S^0(X) - S^T(X)}{T}$$

This quantity is ≥ 0 but it is nontrivial, *i.e.*, $e(X) > 0$, only if $S^T(X) \to \infty$ when $T \to \infty$. So, we cannot have both a finite entropy $S_\rho(X)$ and a nontrivial entropy production $e(X) > 0$. The current evidence [5],[6],[2] is that the projection ρ_X of the NESS ρ to a finite region X is absolutely continuous (at least if X is disjoint from the region where an external force ξ is acting) and that $e(X) = 0$. It does not appear impossible at this time that $\check{e}(X)$ (which is $\geq e(X)$) yields a nontrivial definition of entropy production in the region X. (Note also that $\check{e}(X)$ is a subadditive function of X, while $e(X)$ is superadditive). The problem, however, is wide open. For our Class (3) (quantum spin systems) we have $\check{e}(X) = e(X) = 0$ because $\check{S}^T(X)$ and $S^T(X)$ are bounded.

4 Discussion.

Let us again stress that our discussion of nonequilibrium has been restricted to transport (in fact heat transport), disregarding chemical reactions, metastability, etc. Also, we have focussed on nonequilibrium steady states, and ignored transient phenomena.

Boltzmann had a clear physical idea of why entropy increases in nonequilibrium processes. He was able to implement this idea for gas dynamics (the H-theorem) by ignoring recollisions, and this has led to a rigorous result (Lanford [13]). A rigorous mathematical formulation of entropy production is also possible when an IK thermostat is used. Unfortunately, it remains unclear if a local entropy production $\check{e}(X)$ can be defined nontrivially for infinite classical systems. (For quantum spin systems, the evidence is that such a definition is not possible).

The importance of identifying physical quantities in models of nonequilibrium is shown by the extraordinary success of the Fluctuation Theorem, based on the use of the IK thermostat and the identification of entropy production with volume contraction in phase space. The possibility of identifying a nontrivial local entropy production in infinite systems remains an important challenge. Perhaps progress on this question may be obtained by numerical studies of subsystems of finite systems with IK thermostats and an external force (as indicated in [19]).

References.

[1] L. Andrey. “The rate of entropy change in non-Hamiltonian systems.” Phys. Letters **11A**,45-46(1985).

[2] F. Bonetto, A. Kupiainen, and J.L. Lebowitz. “Absolute continuity of projected SRB measures of coupled Arnold cat map lattices” Ergod. Th. Dynam. Syst. **25**,59-88(2005).

[3] O. Bratteli and D.W. Robinson. *Operator algebras and quantum statistical mechanics* **2**, second edition. Springer, Berlin, 1997.

[4] S.R. de Groot and P. Mazur. *Nonequilibrium thermodynamics.* Dover, New York, 1984.

[5] J.-P. Eckmann, C.-A. Pillet, and L. Rey-Bellet. ”Nonequilibrium statistical mechanics of anharmaonic chains coupled to two baths at different temperatures” Commun. Math. Phys. **201**,657-697(1999).

[6] J.-P. Eckmann, C.-A. Pillet, and L. Rey-Bellet. ”Entropy production in non-linear, thermally driven Hamiltonian systems” J. Stat. Phys. **95**,305-331(1999).

[7] D.J. Evans, E.G.D. Cohen, and G.P.Morriss. “Probability of second law violations in shearing steady states.” Phys. Rev. Letters **71**,2401-2404(1993).

[8] D.J. Evans and G.P. Morriss. *Statistical mechanics of nonequilibrium fluids.* Academic Press, New York, 1990.

[9] G. Gallavotti. “Nonequilibrium statistical mechanics (stationary): overview” pp. 530-539 in *Encyclopedia of Mathematical Physics* (ed. J.-P. Françoise, G.L. Naber, Tsou Sheung Tsun),Vol **3**, Elsevier, 2006.

[10] G. Gallavotti and E.G.D. Cohen. “Dynamical ensembles in stationary states.” J. Statist. Phys. **80**,931-970(1995).

[11] W.G. Hoover. *Molecular dynamics.* Lecture Notes in Physics **258**. Springer, Heidelberg, 1986.

[12] V. Jakšić and C.-A. Pillet. ”On entropy production in quantum statistical mechanics” Commun Math. Phys. **217**,285-293(2001).

[13] O.E. Lanford. “Time evolution of large classical systems.” pp. 1-111 in Lecture Notes in Physics. **38**, Spinger, Berlin, 1975.

[14] J.L. Lebowitz. “Boltzmann’s entropy and time’s arrow.” Physics Today **46**, No 9,32-38(1993).

[15] H.A. Posch, and W.G. Hoover. ”Large-system phase-space dimensionality loss in stationary heat flows” Physica D**187**,281-293(2004).

[16] D. Ruelle “Entropy production in quantum spin systems.” Commun. Math. Phys. **224**,3-16(2001).

[17] D. Ruelle “Extending the definition of entropy to nonequilibrium steady states.” Proc. Nat. Acad. Sci. **100**,3054-3058(2003).

[18] D. Ruelle ”Nonequilibrium statistical mechanics and entropy production in a classical infinite system of rotators.” Commun. Math. Phys. to appear.

[19] S.R. Williams, D.J. Searles, and D.J. Evans. ”Independence of the transient fluctuation theorem to thermostatting details” Phys. Rev. E **70**,066113–1-6(2004).