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On the Thermodynamics of a Room, a Heater and a Window

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ABSTRACT

In depth discussion of thermodynamics of a familiar system made of a room, a heater and a window reveals the rich complexity underlying the deceptively simple assumption of local thermodynamic equilibrium. It displays also the failure of available approaches to non-equilibrium thermodynamics.

Keywords: Non-equilibrium thermodynamics; stability; local thermodynamical equilibrium.

1. INTRODUCTION: GUESS WHO'S COMING TO BE STABLE

Why do spaghetti form stable vortices when cooking? Chandrasekhar has proven that spaghetti-tracked, stable convection cells satisfy a variational principle. Why do quiescent prominences arise in the solar corona? Taylor's principle rules many stable, self-organised plasmas. When it comes to stability criteria for self-organised, far-from-equilibrium structures in fluids and plasmas, the scientific literature is crowded with many different, problem-dependent, sometimes unproven principles. To date, the search for an Ariadne's thread in this labyrinth required introduction of ad hoc hypotheses, which are less evident than the criteria themselves. Following a suggestion of Prigogine, here we point at a common feature of many such structures: at all times, the relationships among thermodynamic quantities in a small mass element are the same as in real thermodynamic equilibrium. This feature constrains the evolution of the system, including possible relaxation to a final, stable state. The resulting constraints are the looked-for Ariadne's thread: many well-known stability

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criteria are retrieved as particular cases, from Chandrasekhar's and Taylor's principles to Malkus' principle for Couette flow and Paltridge's principle in Earth's atmosphere. We start with the qualitative discussion of a simple system, made of a room with a heater and a window. In spite of its deceptive simplicity, this example encompasses all relevant results to be applied in the following. It allows us to discuss the failure of most attempts to write down a single, general-purpose variational description of stability far from thermodynamic equilibrium.

2. MUCH ADO FOR NOTHING

In spite of the rooted skepticism of the few [1], the decade-long search of the Holy Grail of non-equilibrium thermodynamics –a universal variational principle for the stability of systems far from thermodynamic equilibrium, analogous in power and generality to the Second Principle for systems at thermodynamic equilibrium–seemed to be near a glorious end after the astonishing results of Belgian and Dutch researchers: De Donder's chemical affinity, Onsager's symmetry relationships, Prigogine's dissipative structures and the like –for a historical review [2]. Today, the field is utterly ignored by the vast majority of physicists; most of the latter agree wholeheartedly with Jaynes' sharp judgment [3]: if we have enough information to apply a variational principle far-from-equilibrium with any confidence, then we have more than enough information to solve the steady-state problem without it. Admittedly, the quest for stability remains of utter relevance; however, practically no researcher takes on this problem but with help of direct analysis of the equations of motion, on a case-by-case basis. Nevertheless, people who were not satisfied with this usually cumbersome approach have been able to find through trial and error a host of variational principles for relaxed states in many fields of physics, and most of them still need rigorous proof. We guess there is plenty of room for thermodynamics here. By far and large, however, the present mistrust is well justified: attempts to derive the principles under discussion are so far unconvincing since they often require introduction of additional hypotheses, which by themselves are less evident than the proved statements [4].

Remarkably, most of the properties usually dealt with when investigating the stability of a thermodynamically open system –namely, the stability of temperature profiles and of the large-scale structures in convective motion– are retrieved in the analysis of a simple, familiar system of every-day life: a room with a heater and a window. In the following we are going to show that this system may usually relax to stable states where some variational principles are satisfied –on average at least. To this purpose, we just invoke the approximation of 'local thermodynamical equilibrium' (LTE), to be explained below. Our arguments are qualitative: for rigorous proofs see [5]. Then, we show that none of the would-be Holy Grails which are available in the literature is able to describe our room with its heater and its window, in spite of the simplicity of this system. Finally, we show that many well-known variational principles for the relaxed states of different physical systems are but particular case of the results obtained for our room.

3. THE ROOM, THE HEATER AND THE WINDOW

A room has a window and contains a heater. Initially the window is closed. For the moment, we imagine that the window remains closed all the time. When the power is switched on, the heater starts heating the room. Some heat is exchanged with the external world through conduction across the window. After a while, the temperature T relaxes to a steady value

$T(\mathbf{x})$ everywhere. Intuitively, we expect that $T(\mathbf{x})$ is maximum near the heater. Even if obvious, this conclusion deserves further attention.

Let us introduce the (non-negative) heating power density $P_h(\mathbf{x})$, which of course attains a maximum in the region of space occupied by the heater. In the present example $P_h(\mathbf{x})$ vanishes outside the heater. However, we may easily remove this assumption. In fact, nothing essential changes if we assume $P_h(\mathbf{x})$ to vanish nowhere: think e.g. of a great number of microscopic heaters scattered all across the room. In the following we suppose the steady-state value of the total heating power $\int P_h(\mathbf{x})\, d\mathbf{x}$ to attain a known value P_{TOT} (the domain of integration is the room volume). Maximization of $T(\mathbf{x})$ where $P_h(\mathbf{x})$ is larger –i.e., near the heater– is equivalent to reduce $T(\mathbf{x})^{-1}P_h(\mathbf{x})$ everywhere, hence leads to:

$$\int T(\mathbf{x})^{-1}P_h(\mathbf{x})\, d\mathbf{x} = \text{minimum with the constraint } \int P_h(\mathbf{x})\, d\mathbf{x} = P_{TOT} \quad (1)$$

We denote with $a_0(\mathbf{x})$, $a_1(\mathbf{x},t)$ and $<a> (\mathbf{x},t) = \lim_{t'\to\infty} (1/t') \cdot\int_t^{t+t'} dt''\, a(\mathbf{x},t'')$ the steady-state value of the generic quantity a, a fluctuation near $a_0(\mathbf{x})$ (occurring on small time-scales and short spatial scales) and the time-average of a respectively. In particular, $<a_0(\mathbf{x})> = a_0(\mathbf{x})$ and $<a_1(\mathbf{x},t)> = 0$, i.e. steady-state values are time-averages which smear out fluctuations. Accordingly, we identify 'steady-state values' with 'time-averaged values'; for example, (1) is equivalent to a result we are going to invoke again and again below:

$$<\int T(\mathbf{x})^{-1}P_h(\mathbf{x})\, d\mathbf{x}> = \text{minimum with the constraint } <\int P_h(\mathbf{x})\, d\mathbf{x}> = P_{TOT} \quad (2)$$

The decomposition $a = a_0 + a_1$ discussed above makes (2) to be equivalent to:

$$<\int (T(\mathbf{x})^{-1})_1 P_h(\mathbf{x})\, d\mathbf{x} >> \quad 0 \quad (3)$$

provided that $<\int P_h(\mathbf{x})\, d\mathbf{x}> = P_{TOT}$, as usual by now. According to (3), any heating (cooling) process leads to a decrease (increase) of $P_h(\mathbf{x})$. This result is but an example of Le Chatelier's principle [6], which states that an external interaction brings about processes which tend to reduce the effect of this interaction. In turn, Le Chatelier's principle follows from the Second Principle of thermodynamics when applied to a body at LTE, i.e. a body – e.g. a small mass element of a fluid, a small volume element of our room etc.– which is itself at thermodynamical equilibrium, though not necessarily at thermodynamical equilibrium with the medium surrounding it. Once LTE is verified everywhere in the room, validity of (2) requires no further assumption on kinetic physics, turbulence, heat transport etc.

According to Prigogine [7], LTE is a necessary condition for the feasibility of any thermodynamic description of a system. In particular, LTE means that means that all familiar thermodynamic quantities like temperature, pressure etcremain well defined and all familiar thermodynamic relationships among such quantities remain valid in the body, even its temperature, its pressure etc. differ from the corresponding quantities in the surrounding environment. LTE is a common tool e.g. in fluid mechanics [8]; as for plasmas, see Refs. [9], [10] and [11]. Eventually, LTE can only be justified by comparison with experiments.

Our discussion shows that (2) holds regardless of the detailed heating mechanism ruling $P_h(\mathbf{x})$ in a small volume element of the room centered at $\mathbf{x}$, including e.g. combustion, viscous heating, nuclear fission or fusion, Ohmic heating of an electric resistor, radioactive decay… Nothing is said on the actual origin of the power supplied to the heater: it may be either internal to the room (e.g. burning coal) or external (a plug connecting an electric heater to the grid). Moreover, (2) provides us with a link between the distributions of temperature and heating power density in a stable, steady state even if we do not know the exact mechanism of heat transport (including e.g. the values of thermal conductivity, radiation opacity, or heat exchange coefficients in the room).

In spite of its generality, (2) is far from providing us with a complete description of the relaxed configuration of our room. In fact, such description requires further information like e.g. the equation of state of the air in the room, the boundary values of T at both the heater, the walls and the window, etc. Of course, different stable profiles of $T(\mathbf{x})$ and $P_h(\mathbf{x})$ may exist, depending on the information listed above.

Remarkably, however, (2) is a necessary condition for the stability of the state our room has relaxed to. (This is scarcely surprising, as the second principle itself describes a stable state). In fact, should (2) be violated, there a region would exist somewhere in the room where e.g. a small increase of $T(\mathbf{x})$ would raise $P_h(\mathbf{x})$, thus triggering a positive feedback which would drive the system far from the initial state. Once LTE is satisfied, the Second Principle–through Le Chatelier's principle– tells us that if a steady, stable state exists for our room then it satisfies (2). The actual description of the room is provided by the balance equations of mass, momentum and energy, including turbulence, radiative effect etc. Stable steady solutions of these equations are those steady solutions which satisfy also (2). The latter condition may therefore be useful when bringing forward the –often cumbersome– analysis of stability of the solutions of the equations of motion.

The quantity $<\int T(\mathbf{x})^{-1}P_h(\mathbf{x})\, d\mathbf{x}>$ minimized in (2) has the dimension of [entropy/time], and may be considered as the amount of entropy produced per unit time by the heating processes inside the room. Remarkably, it differs from the total amount of entropy produced per unit time by all irreversible processes. Again, this point deserves further discussion.

Let a small, helium-filled balloon be inside the room at the initial time, and let a very small hole be on the balloon, so that the helium may leak slowly. After a while, the helium diffuses freely across the room. This is definitely an irreversible process which raises entropy. However, the corresponding entropy production is related in no way to the heating process in the heater and leaves therefore (2) unaffected. As we shall see below, different contributions to the entropy balance enjoy different properties in a stable state. This point is usually overlooked in the literature.

4. THROUGH THE LOOKING GLASS

So far we have dealt with the heater. Now, let us discuss the window. As far as it remains closed, it prevents mass from being exchanged between the room and the external world. Nevertheless, radiation and conduction of energy are still possible across the window. Actually, in a stable, steady state they must occur. In fact, the total amount of energy in the room remains constant in such state. Accordingly, the power input $\int P_h(\mathbf{x})\, d\mathbf{x}$ supplied by the heater to the room is to be compensated by a power loss across the window. This loss occurs either through radiation or conduction as convection is forbidden; the corresponding heat flux $\mathbf{q} = \mathbf{q}(\mathbf{x})$ across the window satisfies the normalization condition

$$<\int \mathbf{q}(\mathbf{x}) \cdot d\mathbf{a}> = <\int P_h(\mathbf{x})\, d\mathbf{x}> \qquad (4)$$

(the domain of integration in the L.H.S. is the window surface).

Now, let us introduce two auxiliary, dummy assumptions: everywhere on the window a) **q**(**x**) is uniform and b) P_h(**x**) attains a minimum. (We will drop both assumptions below). Minimization in (2) requires that the larger P_h(**x**) the larger T(**x**), hence assumption b) implies that 1/T(**x**) is maximum at the window. Accordingly, assumption a) and (2) lead to:

$$<\int T(\mathbf{x})^{-1}\mathbf{q}(\mathbf{x}) \cdot d\mathbf{a}> = \text{maximum with the constraint } <\int P_h(\mathbf{x})\, d\mathbf{x}> = P_{TOT} \quad (5)$$

Four remarks are at hand. Firstly, we may drop assumption a). In fact, we may consider a single window with non-uniform **q**(**x**) as a set of many, small windows –each with its own uniform value of **q**(**x**); then, we repeat our argument for each small window, add up the contributions of all windows and obtain once again (5) as a result. Secondly, (4) makes P_h(**x**) to disappear from (5) identically, i.e. (5) contains no information concerning either the actual position of the heater or the heating process in the heater. Physically, this is far from surprising: $T(\mathbf{x})^{-1}\mathbf{q}(\mathbf{x})$ has the dimension [entropy/(time·surface)] of an entropy flux related to heat radiation and conduction, and these physical processes have nothing to do with the heating process. Accordingly, we may drop assumption b). Thirdly, the quantity maximized in (5) has the dimension of [entropy/time], and may be considered as the time-averaged total amount of entropy received –through conduction and radiation only– per unit time by the external world from the room. Finally, LTE is the only crucial assumption for the validity of (5); the relative weight of conduction and radiation is not relevant.

5. COMING UP WITH AIR

Once the room has relaxed to a configuration described by (2)-(5), let us open the window. Convection starts across the window. Generally speaking, convection may be turbulent, and turbulence is intrinsically unsteady. Moreover, we do not expect convection to disappear as time goes by: as far as the temperature gradient across the window is large enough, convective cells never stop rotating. In contrast, convection may play a crucial role in keeping the time-averaged temperature gradient approximately constant. Both the time-scale and the spatial scale of convective cells may be far from negligible, and it is therefore not possible to dismiss convective cells just as fluctuations in the sense of our discussion above. Accordingly, it is difficult to say that the system relaxes to a final steady state.

All the same, we expect that the system evolves towards a configuration where $<a>(\mathbf{x},t)$ do not depend on time. We take this definition as a valid definition of ‘relaxed state’ above. In order to assure that the definition of $<a>(\mathbf{x},t)$ remains meaningful during the relaxation, we must take care that the auxiliary time t’ in the definition of $<a>$ is much larger than the typical time-scale of both small-scale fluctuations and of convective cells but remains much shorter than the characteristic time-scale of relaxation. We are going to investigate this point further below. For the moment, we are going to speak of ‘relaxed state’ instead of ‘steady state’, and recall that (2) plays the role of necessary condition of stability If the relaxed state (if any such state exists).

After a while, the room evolves again towards a new relaxed state, with a steady (on average) distribution of temperature. Since (2) is concerned with heating processes only, it remains valid. However, a new physical phenomenon (convection) acts at the window, correspondingly, we expect that both T and **q** are affected and that (5) holds no more.

In order to understand the role of convection across the window, we recall that entropy is an additive quantity, so that convection transports entropy with a flux ρ s **v** (which has again the dimension [entropy/(time·surface)]) where $\rho = \rho(\mathbf{x})$, $s = s(\mathbf{x})$ and $\mathbf{v} = \mathbf{v}(\mathbf{x})$ are the mass density, the entropy per unit mass and the velocity of a small mass element respectively. The quantity $<\int (\rho s\mathbf{v})(\mathbf{x})\cdot d\mathbf{a}>$ is therefore the time-averaged, total amount of entropy received –through convection only– per unit time by the external world from the room. Correspondingly, the quantity $<\int (T^{-1}\mathbf{q} + \rho s\mathbf{v})(\mathbf{x})\cdot d\mathbf{a}>$ is the time-averaged, total amount of entropy received per unit time by the external world from the room.

On one side, convection is an irreversible phenomenon, i.e. convection-related entropy production is non-negative; it occurs continuously as convection never disappears, and vanishes only if no convection occurs. On the other side, however, the time-averaged overall content of entropy of the room is constant in steady state.

These conclusions do not contradict each other only if convection adds a further, non-negative contribution to the time-averaged amount of entropy received by the external world per unit time above the contribution $<\int (T^{-1}\mathbf{q})(\mathbf{x})\cdot d\mathbf{a}>$ of radiation and conduction. To put it in other words, the final effect of window opening on the final, relaxed state is to add a non-negative term to the time-averaged amount of entropy received by the external world per unit time.

Now, we are free to imagine our room inside another, larger room with a window, inside another room with a window… like Russian dolls, indefinitely. Our original room is the only on with a heater, so that P_{TOT} remains unchanged. With no loss of generality we may suppose that the external world is always infinitely larger than this system of nested rooms, regardless of the actual number of rooms, so that the latter number leaves the domain of integration of the surface integral in (5) unaffected.

Let us open all these windows sequentially, each after another, starting from our original room outwards. On one side, any opening of a window adds a non-negative term to the time-averaged total amount of entropy received by the external world per unit time. On the other side, however, the latter quantity is both finite and constant in a relaxed state. These conclusions do not contradict each other only if the value of $<\int (T^{-1}\mathbf{q} + \rho s\mathbf{v})(\mathbf{x})\cdot d\mathbf{a}>$ in the relaxed state has attained a maximum. Then, (5) is replaced by:

$$<\int (T^{-1}\mathbf{q} + \rho s\mathbf{v})(\mathbf{x})\cdot d\mathbf{a}> = \text{maximum with the constraint} <\int P_h(\mathbf{x})\, d\mathbf{x}> = P_{TOT} \quad (6)$$

Relationship (6) generalizes (5) to the case where convection occurs between the room and the external world. It concerns only the total amount of entropy received by the external world from the room, and holds regardless of the relative weight of convection, conduction and radiation. As anticipated, it holds even if more than one window is present; in this case, the domain of integration in (6) is the union of the surfaces of all windows. It holds even if no heating at all occurs anywhere in the room. In this case, $P_{TOT} = 0$ and (4) dictates that $\int \mathbf{q}(\mathbf{x})\cdot d\mathbf{a} = 0$. (This is e.g. the case of a room with no heater and two windows: where the heat flux coming into the room through the first window compensates the heat flux coming from the room outwards through the second window). Finally, (6) holds regardless of the number (possibly zero) of open windows.

Remarkably, (6) is a maximum principle, while (2) is a minimum principle. Even if both results are necessary conditions for the stability of the same relaxed state, there is no contradiction as (2) and (6) refer to different phenomena: entropy production through heating vs. entropy exchange with the external world respectively. It follows that the attempts of some theory to maximize (or minimize) the same quantity for all irreversible phenomena in a relaxed state are doomed to fail.

So far, we assumed nothing on the frequency spectrum of a1. Accordingly, both (2) and (6) hold even if $a_1 \propto \exp(2\pi it/\tau)$ with period τ<< the characteristic time of relaxation of our system room + heater + window. (We may imagine that there is a fan in our room, whose blades keep on rotating at high frequency $1/\tau$ even after relaxation has occurred). In this case, the relaxed configuration is a periodically oscillating state.

This generalization is far-reaching. Firstly, the fact that both (2) and (6) deal with time-average values only allow both of them to hold even if the walls are not exactly still, but moving on a time-scale << the characteristic time of relaxation: any such motion leaves (2) and (6) unaffected, as its effect disappears after time averaging. Secondly, should the system undergo a spontaneous transition (mathematicians call it 'bifurcation') from a steady state to an oscillatory state, or from an oscillatory state to another oscillatory state with different period, (2) and (6) would provide a selection rule: the system selects the configuration which minimizes the time-averaged amount of entropy produced by heating per unit time, or, equivalently, which maximizes the time-averaged amount of entropy received per unit time by the external word from the system.

6. THE GARDEN OF FORKING PATHS

We have seen that even a simple, familiar system made of a room, a heater and a window exhibits a surprisingly rich behaviour, when stability of the relaxed state of the system is considered. The starting point is the LTE assumption, which allows the Second Principle to hold locally, leading to Le Chatelier's principle in a small element of the system. In turn, Le Chatelier leads to the stability criteria (2) and (6).

Of course, there is nothing special in our room. The heating power density $P_h(\mathbf{x})$ may be distributed in space, and its physical origin does not affect our results. The same holds for the detailed physical mechanisms underlying $\mathbf{q}(\mathbf{x})$, or the pattern of convective cells, or the chemical composition of our system and the equations of state of the chemical species which are present in it. Then, none of the above details affect validity of (2) and (6).

Straightforward inspection [5] shows that our results lead —as particular cases— to many criteria of stability for relaxed states in hydrodynamics, plasma physics and thermoacoustics, which have been often suggested in the literature without rigorous proof in order to cope with experiments. The criterion of stability to be adopted depends on the particular problem. Not surprisingly, for isolated systems we retrieve maximization of total entropy at thermodynamic equilibrium. Each criterion of stability takes the form of—or is a consequence of— a variational principle: maximization or minimization, depending on the problem. In agreement with [12] and in contrast with [13], we obtain that characterization of systems far from equilibrium, e.g., by maximum or minimum entropy production is not a general property but is reserved to special systems. In each case, a relaxed state solves the steady-state equations of motion (in order to be a physically allowable steady state) *and* satisfies the relevant stability condition (in order to be stable). If the latter reduces, e.g., to a constrained minimization, the former adds new constraints -see e.g. [9].

The list of the stability criteria retrieved as particular cases of (2) and (6) includes: i) maximization of the entropy exchanged with the external world through convection per unit time (postulated by Ref. [12] and [14] in strong shock waves and in detonation waves respectively); ii) maximization of the rate of entropy supplied to the surrounding environment through conductive and/or radiative energy transport (applied by Paltridge [15] and Ozawa et al. [16][17] to the large scale structure of the general circulation of Earth's atmosphere and ocean and strongly turbulent convection between parallel walls at different temperatures respectively; iii) minimization of adverse temperature gradient with the constraint of given heating power, a variational property which Chandrasekhar [18] shows to be enjoyed e.g. by Bénard convection cells at low Rayleigh number; iv) maximization of total rate of viscous dissipation per unit mass—with the constraint of fixed mean macroscopic velocity—in the turbulent, incompressible, sheared flow between parallel walls at the same temperature, postulated by [19]; v) Helmholtz and Kortweg's minimization of viscous power for incompressible, viscous fluids, with $\mathbf{v} = 0$ everywhere at the boundary and uniform T across the fluid [20]; vi) Kirchhoff's minimization [21] of Ohmic heating power—with the constraint of charge conservation—for steady currents flowing across electrical conductors with uniform resistivity and no turbulence; vii) Rayleigh's stability criterion in thermoacoustics [22].

So far, we have not discussed regularly oscillating states explicitly. In thermoacoustics, experimenters have reported that ii) rules also the onset of oscillations in their experimental set-up [23], and acts also as a selection rule between different oscillating states. To the author's knowledge, this is the first experimental observation of the thermodynamical counterpart of a bifurcation between different limit cycles, in full agreement with the original suggestion of [24], and confirms our extension of the concept of 'relaxed configuration' from steady to periodically oscillating states.

Finally, vi) reduces to Steenbeck's variational principle [25] V = min. and to Taylor's principle (minimization of magnetic energy with given magnetic helicity) [26] in the particular cases of a free-flowing, radiation-cooled arc with voltage fall V and of a turbulent, relaxed, T >KeV, large-Hartmann-number plasma with no large stabilizing external magnetic field and negligible ∇T respectively.

7. MUCH ADO FOR NOTHING - AGAIN

Historically, stability of relaxed configurations far from thermodynamical equilibrium has been investigated with the help of two variational principles concerning the rate of entropy production due to all irreversible phenomena: Prigogine's minimum entropy production principle and Onsager and Machlup's least dissipation principle. (Both principles apply to steady states only; Tykodi [27] has postulated the extension of the minimum entropy production principle to oscillating states ($a_1 \propto \exp(2\pi i t/\tau)$) without proof). We do not discuss here these principles –see [28] for a thorough discussion. For our purpose, it is enough to say that each principle describes stability against a different sets of perturbations, concerning the so-called 'thermodynamical forces' and 'fluxes'. The former and the latter are derivatives of entropy and derivatives of the entropy production respectively. The validity of both principles requires that LTE holds, that thermodynamic forces are linear combinations of thermodynamic fluxes, with the coefficients ('phenomenological coefficients') which form a symmetric matrix. (Linearity justifies the familiar name of 'linear non-equilibrium thermodynamics', or LNET). In turn, this ('Onsager') symmetry requires that the phenomenological coefficients are constant and that the thermodynamic flows are time derivatives of physical quantities [6]. Symmetrically, in continuous systems Onsager's symmetry requires also that thermodynamic forces are gradients of physical quantities [2].

Formally, LNET is a well-developed theory, with far-reaching implications e.g. in solid state physics [29]. However, the consequences of its uncritical application to problems where the fundamental assumptions underlying Onsager' symmetry do not apply are catastrophic. Heat conduction provides a crystal-clear example of an irreversible, far-from-equilibrium phenomenon where LNET fails. The amount of entropy produced by heat conduction per unit time and volume is $\mathbf{q}\cdot\nabla(1/T)$. Since the thermodynamical force must be the gradient of a physical quantity, a natural choice for the thermodynamical force is just $\nabla(1/T)$. Accordingly, **q** should be the time derivative of some physical quantity. Indeed, the corresponding mechanical quantity, the mass flow, is related (through mass balance) to the time derivative of the total quantity of mass inside a given volume. Carnot would have suggested that **q** is related (through some form of heat balance) to the time derivative of the total mass of Lavoisier's caloric inside a given volume. But Joule's experiments show that no caloric exists, in contrast with Carnot's own ideas. Indeed, it is possible to show that **q** is just the difference of different contributions to the total energy balance [8] and is therefore the time derivative of *nophysical quantity*. This result prevents also any different choice of thermodynamical force and flux inside $\mathbf{q}\cdot\nabla(1/T)$ from supporting LNET validity.

LNET fails whenever heat conduction is involved. Its predictions are indisputably wrong even in the simplest 1-dimensional problem of heat conduction. For example, for uniform thermal conductivity LNET predicts that $\Delta(1/T) = 0$, in contrast with Fourier' heat equation [28] –see also [3] for further counterexamples. A fortiori, LNET is of no use in our room. Much worse, LNET impact on the research in controlled nuclear fusion –where Onsager and Machlup's principle has been postulated when describing heat transport in toroidal plasmas [30]– has been unfavourable, to say the least.

Of course, Prigogine and co-workers [7] were perfectly aware of the limitations due to the requirement of Onsager symmetry. In a seminal paper [24] the impact of LTE on the evolution of a small mass element of a fluid mixture of many chemical species is discussed, where no Onsager symmetry is invoked. The consequences of this work are far-reaching, and are discussed in depth in [5]. In the particular case where entropy depends on internal energy and particle density only and for given values of the fluxes of matter end energy across the boundaries, it turns out that a quantity exists, the so-called 'excess entropy production' [2] whose positiveness is a necessary condition for the stability of steady states. The excess entropy production is defined as the increase in entropy production due to a perturbation. Prigogine's attempt to broaden the narrow domain of validity of the original result [31] has been rejected by Lavenda [32] who has shown that even if the sign of excess entropy production is known, in the general case (e.g. in our room) stability depends on the actual eigenvalues of the linearized equations of motion.

In turn, Lavenda's 'quasi-thermodynamic approach' (QTA) [32] postulates that Onsager and Machlup's least dissipation principle holds even beyond the domain of validity of LNET. QTA requires that the system is ruled by the equations of motion of a generalized, forced, linear harmonic oscillator with constant coefficients. The interpretation of the principle of least dissipation will henceforth be mechanical in nature. Extension of QTA to continuum is possible, but still relies on the assumption that the phenomenological coefficients are constant. The particular case of constant mass density is discussed in Ref. [33]. In spite of these limitations, however, QTA applies successfully to a particular non-linear problem – the limit cycle of a Van der Pol oscillator [34] – provided that the motion behaves as if it were periodic during any single period, whereas the effects of dissipation are only noticeable over the longer space-time of evolution. Of course, our room satisfies none of these assumptions. Quite independently, Ziegler [35] invokes LTE explicitly and postulates what he calls 'orthogonality principle' which is basically equivalent to maximization of entropy production at fixed thermodynamical forces. According to the discussion in [4], Ziegler's principle has its statistical substantiation only if the deviation from equilibrium is small, which is definitely not the case of our room.

This rather frustrating series of failures may suggest that the problem lies in the common assumption of all the proposals discussed so far: LTE. For example, the equations of motion in many physical systems show that different quantities evolve with different time-scales and spatial scales; this result does not rely on LTE. Accordingly, it is at least conceivable that relaxation (if any) satisfies one of the following scenarios: either 'selective decay' or 'maximal entropy' –for an excellent review, see [36]. The selective decay hypothesis is characterized by the following. If one considers the `ideal invariants' of the system and admits a small amount of dissipation, it is often found that one of the invariants is `better conserved' or more rugged than others. If one minimizes the expression for the poorly conserved invariant subject to the constraint that the rugged invariant is conserved using the technique of Lagrange multipliers, an Euler equation for the field variables in the relaxed state results. The Lagrange multiplier is the ratio of the poorly conserved invariant to the ruggedly conserved one. Typically, selective decay applies to two-dimensional Navier-Stokes flows (2D NS) of enstrophy-energy for two-dimensional Navier-Stokes flows (2D NS), to two-dimensional magnetohydrodynamics (2D MHD) and to three-dimensional magnetohydrodynamics (3D MHD). The couples 'rugged invariant vs. poorly conserved invariant' in 2D NS, 2D MHD and 3D MHD are 'enstrophy vs. energy', 'energy vs. mean square vector potential' and 'energy vs. helicity' respectively. In 3D MHD the relaxed state is described by Taylor's principle quoted above [26]. The principle of maximal entropy dictates that the air in a room initially distributed in clumps moves towards smooth uniformity; thermodynamic equilibrium does not admit-large scale structures. However, for a system with a constrained phase space, maximal entropy can generate large-scale structures as a long-lived intermediate state. To apply the principle of maximal entropy, one needs to consider a discrete or quantized version of the field variables. If we have N such quanta of the field (vortices in the case of 2D flow, bundles of flux or current filaments in the case of MHD -see e.g. Refs. [37] and [38]), we consider the number of ways these N quanta can be arranged in a given state (like spins up or down). The most probable state is the one with the most permutations or the highest entropy subject to other constraints (such as conservation of energy and particle number); here entropy is defined as the logarithm of the number of permutations times Boltzmann constant. The description of the system is perfectly analogous to the familiar description of the 2D spin system in statistical mechanics of thermodynamical equilibrium. The maximal-entropy perspective addresses the question: are these observed large-scale, self-organized structures in some sense statistically more probable than other less simple ones?

Now, our room is a thermodynamically open system. Our discussion shows how neither selective decay nor maximal entropy apply *per se* to the relaxed state of our room. The room exchanges either heat (across the closed window) or both heat and mass (across the open window) with the external world. Strictly speaking, however, both selective-decay and maximal-entropy methods apply only to isolated systems. It is for this reason that researchers are used to focus their attention on systems that are freely decaying or are otherwise disconnected from external energy sources. (The situation is far less clear for driven systems, though many of the features found in isolated systems carry over). As for selective decay, in the relaxed state such state dissipation is supposed to be compensated indefinitely, as the value of the rugged invariant is at a constant value in spite of continuous dissipation. As for maximal entropy, in a relaxed state the long-lived large-scale structures are supposed to live not just a long time, but indefinitely. Of course, heat and matter flows from the heater and across the window sustain the relaxed state: but the problem if such support is enough or not to ensure stability is precisely what no approach focused on dissipation in isolated systems may successfully solve. In a nutshell, stability is either to be proven for each problem or to be observed empirically.

Does a description of the relaxed state exist which is as general and problem-independent as thermodynamics and not related to LTE? According to the Extended Irreversible Thermodynamics (EIT) the answer is yes -see Ref. [39] for a review. EIT drops the LTE assumption, and postulates that entropy depends locally not only on internal energy, particle density etc. but also on the heat flux and the viscous stress tensor. Together with Einstein's formula for the probability of fluctuations, EIT leads to predictions which agree with well-known results of kinetic theory near thermodynamic equilibrium. In spite of the alleged independence of EIT from LTE, however, the latter remains somehow involved. For example, the contribution of heat conduction to EIT entropy is basically the product of a relaxation time and the corresponding term in the entropy production rate at LTE. Much worse, T is no more the multiplying factor of the differential of entropy in the first principle of thermodynamics; the familiar formulation of energy balance e.g. in fluid mechanics [8] is therefore contradicted, as well as the relevance of EIT to the physically meaningful description of our room.

Independently, Sawada [13] puts forward a proposal which neither invokes LTE, nor is limited to isolated systems (unlike both selective decay and maximal entropy approaches) nor relies on the constraint of fixed thermodynamical forces (unlike Ziegler) nor modifies the definition of entropy (unlike EIT). Sawada postulates without proof "a principle of maximum increasing rate of the total entropy," even if his arguments lead rather to maximization the amount of entropy exchanged per unit time with external, large heat reservoirs. Sawada supports his maximization procedure with no rigorous argument. Dewar [40] and Niven [41] try to provide formally rigorous, LTE-independent justification of the maximization of entropy production in the relaxed state. This is the so called 'information thermodynamics', or 'MaxEnt'. They start from the results contained in two papers published by Jaynes [42][43], where the author emphasizes a natural correspondence between statistical mechanics (which provides us with the foundation of thermodynamics) and information theory. In particular, Jaynes argues that the entropy of statistical mechanics, and the information entropy of information theory, are principally the same thing. Consequently, statistical mechanics should be seen just as a particular application of a general tool of logical inference and information theory. In most practical cases, the testable information is given by a set of conserved quantities (average values of some moment functions), or, equivalently, but a set of symmetries of the probability distribution. Given testable information, the maximum entropy procedure consists of seeking the probability distribution which maximizes information entropy, subject to the constraints. (Entropy maximization with no testable information takes place under a single constraint: the sum of the probabilities must be one). The principle of maximum entropy can thus be seen as a generalization of the familiar principle of insufficient reason.

MaxEnt has met considerable success outside physics, e.g. in image reconstruction software, natural language processing etc. Basically, it is a brilliant and thought-provoking analysis of our information-gathering processes, a set of rules for identikit-makers. As for physics, both MaxEnt, Ziegler and Sawada's works are examples of Maximum Entropy Production Principles (MEPP). Refs. [4] and [44] provide reviews of MEPP which are focused on Ziegler's work and MaxEnt respectively. MEPP has generally failed to be accepted by the majority of scientists. His tenets have been put in doubt in Refs. [4], [5] and [45]. Admittedly, many experiments on crystal growth [4] confirm MEPP. Moreover, MaxEnthas been applied to atmospheric physics [15][16][46] and to problems with convection [16][17]. Remarkably, however, such results are focused on phenomena which are related to the exchange of entropy across the boundary surface –in agreement with our result (6) with vanishing heating power P_{TOT}. Simply speaking, MEPP does not describe the irreversible heating due to the heater in our room: maximization of entropy production would *minimize* T near the heater.

8. CONCLUSION

We have shown that, in spite of long-time efforts, none of the presently available theories of non-equilibrium thermodynamics is able to provide satisfactorily description of the stability of the relaxed state in our simple system made of a room, a heater and a window. The reason is that our room, although deceptively simple, is a thermodynamically open system where irreversible phenomena occur both in the system's bulk (the heater) and across the system boundary (the window). By the way, this is just what happens in most natural phenomena. In contrast, available theories a) either rely on too restrictive assumptions (LNET, 'excess entropy production', QTA) b) or apply to isolated systems only (selective decay, maximal entropy) c) or postulate just one variational principle for all irreversible phenomena, both in the bulk and across the boundaries (EIT, MEPP).

According to Prigogine et al.'s original intuition [24], LTE itself is enough to put constraints on stable relaxed configurations. More precisely, validity of LTE at all times in an arbitrary small mass element provides us with constraints on the evolution of the system, hence on its possible outcome, the relaxed state. *But such constraints are not necessarily variational principles concerning either entropy or entropy production due to all irreversible processes*. We have written these constraints in the form of relationships (2) and (6); the former and the latter are related to entropy produced by heating in the bulk and entropy transport across the boundary respectively, and take the form of a minimization and a maximization principle respectively. Within this approach, a number of stability criteria in both fluid mechanics, plasma physics and thermoacoustics are retrieved, which in the past have often been postulated without proof in order to cope with experiments.

The search of the Holy Grail is doomed, because there is no need of any Holy Grail. In spite of all claims, no unique variational principle is yet available for stable states far from thermodynamical equilibrium. LTE alone is rich enough to justify all valid macroscopic stability criteria.

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COMPETING INTERESTS

The author declares that no competing interest exists.

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