The fourth law of thermodynamics: steepest entropy ascent

Gian Paolo Beretta
Università di Brescia, Italy

November 18, 2019
To appear in Philosophical Transactions of the Royal Society A

Sommario

When thermodynamics is understood as the science (or art) of constructing effective models of natural phenomena by choosing a minimal level of description capable of capturing the essential features of the physical reality of interest, the scientific community has identified a set of general rules that the model must incorporate if it aspires to be consistent with the body of known experimental evidence. Some of these rules are believed to be so general that we think of them as laws of Nature, such as the great conservation principles, whose "greatness" derives from their generality, as masterfully explained by Feynman in one of his legendary lectures. The second law of thermodynamics is universally contemplated among the great laws of Nature. In this paper we show that, in the past four decades, an enormous body of scientific research devoted to modeling the essential features of nonequilibrium natural phenomena has converged from many different directions and frameworks towards the general recognition (albeit still expressed in different but equivalent forms and language) that another rule is also indispensable and reveals another great law of Nature that we propose to call the «fourth law of thermodynamics». We state it as follows: every nonequilibrium state of a system or local subsystem for which entropy is well-defined must be equipped with a metric in state space with respect to which the irreversible component of its time evolution is in the direction of steepest entropy ascent compatible with the conservation constraints. To illustrate the power of the fourth law, we derive (nonlinear) extensions of Onsager reciprocity and fluctuation-dissipation relations to the far-nonequilibrium realm within the framework of the rate-controlled constrained-equilibrium (RCCE) approximation (also known as the quasi-equilibrium approximation).

1 Introduction

The first and the second law of thermodynamics are considered among the "great laws of Nature." What we mean by this is vividly explained by Feynman in one of his legendary lectures [1]: a "great law of Nature" is a rule, a feature, an assertion that the scientific community has grown to consider an indispensable element of any successful model of a natural phenomenon, at any level of description. The main objective in this paper, is to point to a feature that has emerged from scientific progress in the past few decades and has become a key, indispensable element of all successful models of nonequilibrium natural phenomena. For this reason, we claim that this feature has effectively grown to the level of a new great law of Nature, that we propose to call "the fourth law of thermodynamics."

To make the present discussion as precise as possible, we propose to adopt the following two distinct meanings of the word «thermodynamics»: (1) "Applied Thermodynamics" is the art of modeling the kinematics and the dynamics of physical systems by choosing the most appropriate level of description for the 'application of interest' and implementing/exploiting the general principles/rules/laws that any such model ought to satisfy to guarantee a fair representation of the physical reality it is meant to describe (in the sense of Margenau’s "plane of perceptions" [2]). (2) "Foundational Thermodynamics" is the art of extracting/distilling/identifying such general principles/rules/laws from the successes and failures of the entire body of scientific modeling efforts to rationalize experimental observations.

So, when thermodynamics is understood as the science/art of constructing effective models of natural phenomena by choosing a minimal level of description capable of capturing the essential features of the physical reality of interest, the scientific community has identified a set of general rules that the model must
incorporate if it aspires to be consistent with the body of known experimental evidence. Some of these rules are believed to be so general that we think of them as laws of Nature, such as the great conservation principles, whose “greatness” derives from their generality.

The «first law of thermodynamics» [3, p.30] requires that — regardless of the details of the model assumed to describe a “physical system” A (any physical system) and its “states” — for any two states $A_1$ and $A_2$ in which A is isolated and uncorrelated from the rest of the universe, it must be admissible within the model to devise at least one time evolution in which $A_1$ and $A_2$ are the end states of the system, while the only effect in the rest of the universe is a change in elevation of a weight in a gravity field (or an equivalent work element [4, App.C]). Moreover, for a given weight and gravity acceleration the change in elevation is the same for any such time evolution between states $A_1$ and $A_2$. Such requirement is necessary to support the measurement procedure [3, p.32], illustrated in Figure 1(left), that defines operationally the “energy difference” between any two states in which the system is isolated and uncorrelated. In addition, it implies the additivity of energy differences for noninteracting composite systems, the conservation of energy and, therefore, the energy balance equation.

The «second law of thermodynamics» [3, p.62] requires that — again, regardless of the details of the model assumed to describe a physical system A and its states — for any two states $A_1$ and $A_2$ in which A is isolated and uncorrelated from the rest of the universe, it must be admissible within the model to devise at least one reversible time evolution in which the system starts in state $A_1$ and ends in state $A_2$, while the only effects in the rest of the universe are a change in elevation of a weight in a gravity field and the change from state $R_1$ to state $R_2$ of a thermal reservoir (or heat bath) such as a container with water at the triple point in both states $R_1$ and $R_2$ (for more rigorous definitions see [3, 5, 6]). By “reversible” we mean that the model must admit also a time evolution that returns system A from state $A_2$ back to state $A_1$, while the only effects in the rest of the universe are the return of the weight to its original elevation and the change from state $R_2$ back to state $R_1$ of the thermal reservoir. Such requirement is necessary to support the measurement procedure [3, p.102], illustrated in Figure 1(right), that defines operationally the “entropy difference” between any two states in which the system is isolated and uncorrelated. In addition, it implies the additivity of entropy differences for composite systems in uncorrelated states, the conservation of entropy in reversible processes, the principle of non-decrease of entropy and, therefore, the entropy balance equation.

We emphasize that the present discussion focuses on when a given specific model has been chosen and set for the nonequilibrium problem of interest. This means that a given level and framework of description (e.g., macroscopic, mesoscopic, microscopic, classical, quantum, stochastic) has been chosen together with a specific set of state variables and a specific law for their time evolution, and that all definitions, including those of (local) energy, (local) entropy, and (ir-)reversibility, must be self-consistent within the assumed

---

1By state we generally mean the collection of the values of all the properties at one instant of time, and by property a physical observable defined by a measurement procedure that produces an outcome that depends on a single instant of time.
model. Therefore, the otherwise interesting discussions about how to define rules, such as coarse graining and projection methods, for passing consistently from a given level of description to a more macroscopic one [7, 8, 9, 10], about model reduction techniques [11, 12, 13], or about how to identify rate controlling constraints [14], do not play a role here [4].

The second law is universally contemplated among the great laws of Nature, although no two scientists will tell you what it is in the same way, except when they agree to coauthor a paper (see, e.g., [15, 16, 17, 18, 19, 20, 21, 22, 23, 24] or a book (see, e.g., [25, 26, 27, 28, 29, 30]). Our understanding of the laws of thermodynamics has never stopped evolving over the past two centuries. The initial focus on classical statistics and kinetic theory (Boltzmann), chemical kinetics and equilibrium (van’t Hoff, Gibbs), quantum statistics (Fermi-Dirac, Bose-Einstein), near equilibrium and chemical kinetics (Onsager, Prigogine), shifted in more recent decades towards complex fluids and solids, far nonequilibrium, and small and quantum systems. On and off during this evolution, some of the basic concepts needed to be revisited to adapt/extend their applicability to the new realm of phenomena of interest. Questions like “What is work?”, “What is heat?” [31, 32, 33, 34, 35, 36, 37], “What is entropy?” [15, 16, 17, 18, 19, 20, 38], “What is macroscopic?” [33, 34, 35] have risen to a currently urgent need in the quantum (Q) communities (Q information, Q computing, Q thermal machines, Q fluctuations) [5].

The second law has been stated in many ways over the almost two centuries of history of thermodynamics, and it is not our purpose here to review them. However, our preference goes to the Hatsopoulos-Keenan statement [3, p.62] not only because we have provided rigorous proofs that it entails the better known traditional statements (Kelvin-Planck [3, p.64], Clausius [3, p.134], Carathéodory [3, p.121]), but — quite importantly for the current and recent developments of nonequilibrium and quantum thermodynamics — because we have shown in [32, 33, 34] that the operational definition of entropy supported by this statement is valid not only for the stable equilibrium states of macroscopic systems but also for their nonequilibrium states and it provides a solid basis for its extension to systems with only few particles and quantum systems. We have also shown that when restricted to macroscopic systems in equilibrium (in the sense of what we called “simple model system of stable equilibrium states” [3, Ch.17]) our operational definition of entropy based on the Hatsopoulos-Keenan statement is essentially equivalent to the definition of entropy more recently proposed by Lieb and Yngvason in [35] and is closely related to the various extensions and improvements proposed thereafter [19, 20].

Another important implication of the second law is the “state principle,” which asserts [3, Ch.8]) that the equilibrium states of a system form an \((r+s+1)\)-parameter family, where \(r\) denotes the number of conserved properties in addition to energy and \(s\) the number of control parameters of the Hamiltonian. This assertion, in turn, implies the existence for every system of a concave “fundamental equilibrium relation,” for example, \(S = S_{eq}(E, V, n_1, \ldots, n_r)\), for a system with volume \(V\) as the only parameter and \(r\) different types of independently conserved amounts (denoted by \(n_i\)). The “greatness” of this second-law consequence stems from the fact the existence and concavity must hold for any system, but the functional

---

2 However, from our claim in this paper, namely that the fourth law should apply within any level of description that contemplates dissipation, it follows that coarse graining, projection methods, and other rules to pass from one level to more macroscopic ones should also include the relations that must hold between the two steepest-entropy-ascent metrics that characterize the two related levels of description.

3 As already mentioned, the first law entails the existence of property energy for all states of every “system” by supporting its operational definition [3, p.32] (see also [46, 47, 48]), but it can do so only for models in which the system is well separated from its environment. In the quantum framework this means that the effects of the environment on the system can be modeled via the dependence of the Hamiltonian operator on a set of classical control parameters. Suppose system \(AB\) (Alice and Bob as a couple) is well separated but the influence of Alice on Bob and vice versa is described by a full-fledged interaction Hamiltonian \(V_{AB}\): then the energy of \(AB\) is defined (represented by the mean value of the Hamiltonian \(H_A + H_B + V_{AB}\)) but the individual energies of \(A\) and \(B\) are not! The same issue is faced when \(B\) (Bath) is the environment of \(A\), hence, the difficulties in applying thermodynamic concepts to open systems unless the effects of the full-fledged system-bath interaction can be reduced to a description in terms of local operators such as in the Kraus–Kossakowski–Ingard–Lindblad–Gorini–Sudarshan–Spohn (KKILGSS) models [19, 20, 31, 32, 33, 34] or in the locally-steepest-entropy-ascent (LSEA) models of composite systems [49, 50, 51, 52].

4 Its extendability to correlated states of interacting or non-interacting systems is instead still the subject of intense debate, because the correlation entropy (often called mutual information), similarly to the mean energy of interaction between the subsystems, is a well-defined feature for the overall state of the composite system, but there is no unique nor fundamental recipe to allocate it among the subsystems nor to assign it to the local (reduced, marginal) states of the subsystems, even though in the context of LSEA models we have proposed a possible way in [53, Eq.12], [55, Sec.10], and [60, Eqs.60-61].
dependence of the relation varies from system to system and is in fact what characterizes its equilibrium properties.

By analogy, and to allow full flexibility of formulation, what we propose to call the “fourth law of thermodynamics” is any assertion that — regardless of the specific and technical details that are peculiar to one or the other non-equilibrium theory, or of the prose preferences of the different authors — entails a principle of existence of a metric field, defined over the entire state space of the modeled system, with respect to which the irreversible (dissipative) component of the time evolution of the system (or of each of its subsystems) is steepest entropy ascent (SEA). The functional dependence of the SEA metric on the state variables varies from system to system and is in fact what characterizes its nonequilibrium behavior.

In Sections 2 and 3 we prepare the stage for the detailed formulation of the fourth law in Section 4 and one of its consequences in Section 5.

2 Representation on the nonequilibrium energy–entropy diagram

The second law implies also the well-known “maximum entropy principle,” which states [3, p.119]) that among all the states of the system that (within the given model) share the same (mean) value of the energy, the same values of the external control parameters (if any), and the same (mean) values of the other independent conserved properties (if any), only the (unique) stable equilibrium state has the maximal entropy. Therefore, for example, respectively, for (a) an infinitesimal element of a fluid continuum with energy density \( \hat{\varepsilon} \), concentrations \( \hat{n} \), and entropy density \( \hat{s} \), or (b) a closed and uncorrelated quantum system with mean energy \( \langle E \rangle = \text{Tr}(H\rho) \) and (nonequilibrium) entropy \( \langle S \rangle = -k_B\text{Tr}(\rho \ln \rho) \), the nonequilibrium or non-stable-equilibrium states have entropies strictly smaller than the maximum,

\[
\hat{s} < \hat{s}_{\text{eq}}(\hat{\varepsilon}, \hat{n}) \quad \text{case (a)} \quad \langle S \rangle < \langle S \rangle_{\text{eq}}(\langle E \rangle) \quad \text{case (b)}
\]

This prompts the energy–entropy diagram representation of nonequilibrium states shown in Figure 2. It is obtained by first foliating the full state space of the system with respect to the values of its external control parameters and the mean values of the independent conserved properties other than energy, and then by projecting one of these leaves onto the energy–entropy plane. This representation has been first introduced in [16] and fully exploited and explained in [3]. Recently it has been reintroduced and applied.
in the quantum thermodynamics framework in [33, 64]. Temperature is defined only for the stable equilibrium states: (a) \( T^\text{eq} = \frac{\partial \hat{S}_{\text{eq}}(\hat{e}, \hat{n})}{\partial \hat{e}} \), (b) \( T^\text{eq} = \frac{\partial \langle S \rangle_{\text{eq}}(\langle E \rangle)}{\partial \langle E \rangle} \), and on the energy–entropy diagram it is represented by the slope of the curve representing the fundamental equilibrium relation: (a) \( \hat{s}_{\text{eq}}(\hat{e}, \hat{n}) \), (b) \( \langle S \rangle_{\text{eq}}(\langle E \rangle) \).

The «third law of thermodynamics» asserts that the stable equilibrium state of lowest energy [for the given values of the external control parameters (if any), and the given (mean) values of the other independent conserved properties (if any)] has temperature equal to zero and entropy equal to \( k_B \ln g \) where \( g \) is the degeneracy of the corresponding ground state (see [33, 64]).

The full description of nonequilibrium states requires in general (in any model) a number of independent variables (typically much) larger than for the equilibrium (maximum entropy) fundamental relation. Denoting by \( \gamma \) the state vector, i.e., the full list of such nonequilibrium independent variables, the entropy and the conserved properties (like all other properties) are functions of such variables

\[
\dot{s} = \dot{s}(\gamma) \quad \dot{e} = \dot{e}(\gamma) \quad \hat{n} = \hat{n}(\gamma) \quad \text{case (a)} \quad \langle S \rangle = \langle S \rangle(\gamma) \quad \langle E \rangle = \langle E \rangle(\gamma) \quad \text{case (b)}
\]

and the equilibrium fundamental relation and its differential (Gibbs relation) are, respectively,

\[
\dot{s}_{\text{eq}} = \dot{s}(\gamma_{\text{max}} s(\hat{e}, \hat{n})) \quad \text{case (a)} \quad \langle S \rangle_{\text{eq}} = \langle S \rangle(\gamma_{\text{max}} (\langle S \rangle)) \quad \text{case (b)}
\]

\[
d\dot{s}_{\text{eq}} = \beta^\text{eq} d\dot{e} + \sum_i \lambda_i^\text{eq} d\hat{n}_i \quad \text{case (a)} \quad d\langle S \rangle_{\text{eq}} = \beta^\text{eq} d\langle E \rangle \quad \text{case (b)}
\]

where \( \gamma_{\text{eq}} = \gamma_{\text{max}} s(\hat{e}, \hat{n}) \) and \( \gamma_{\text{eq}} = \gamma_{\text{max}} (\langle S \rangle) \) are the solutions of the respective constrained maximum entropy problems: (a) \( \max_{\gamma} \dot{s}(\gamma) \) subject to \( \dot{e}(\gamma) = \hat{e} \) and \( \hat{n}(\gamma) = \hat{n} \) for given values of \( \hat{e} \) and \( \hat{n} \); and (b) \( \max_{\gamma} \langle S \rangle(\gamma) \) subject to \( \langle E \rangle(\gamma) = \langle E \rangle \) for given value of \( \langle E \rangle \). Of course, in case (a) \( \beta^\text{eq} = \frac{\partial \langle S \rangle_{\text{max}} s(\hat{e}, \hat{n})}{\partial \hat{e}} \) and in case (b) \( \beta^\text{eq} = \frac{\partial \langle S \rangle_{\text{max}} (\langle S \rangle)}{\partial \langle E \rangle} \).

As part of the “art” of choosing the most appropriate level of description, when a detailed description of nonequilibrium states is given in terms of the state variables \( \gamma \) and includes a detailed kinetic law for their time evolution, it is often possible to identify a small set of slow, rate-controlling (possibly coarse grained)

---

5This representation is conceptually different from (and must not be confused with) the representation on the equilibrium energy–entropy diagrams introduced by Gibbs [61] and used, e.g., in [62, Par.20] and [63, Fig.1.1], which refer and are restricted to the equilibrium states of a system or fluid element in contact with a thermal bath.
properties, related to the “bottlenecks” of the system’s detailed kinetics. We call them the “rate-controlled constrained-equilibrium” (RCCE) constraints and denote them by $\bar{a}(\gamma)$ in case (a) or $(A)(\gamma)$ in case (b).\(^6\)

The RCCE approximation consists of assuming that the state evolves along the family of maximum entropy manifolds (the blue curves in Figure 3) parametrized by the values of the rate-controlling constraints and the conserved properties

$$\gamma \approx \gamma_{\text{RCCE}} = \gamma_{\text{max}} s(\dot{e}, \dot{n}, \dot{a}) \quad \text{case (a)} \quad \quad \gamma \approx \gamma_{\text{RCCE}} = \gamma_{\text{max}} \langle S \rangle(\langle E \rangle, \langle A \rangle) \quad \text{case (b)}$$

(5)

where, in terms of Lagrange multipliers $\beta, \lambda_i, \chi_k$, the RCCE state $\gamma_{\text{RCCE}}$ is the solution of

$$\frac{\delta \dot{s}}{\delta \gamma} = \beta \frac{\delta \dot{e}}{\delta \gamma} + \sum_i \lambda_i \frac{\delta \dot{n}_i}{\delta \gamma} + \sum_k \chi_k \frac{\delta \dot{a}_k}{\delta \gamma} \quad \text{case (a)} \quad \quad \frac{\delta \langle S \rangle}{\delta \gamma} = \beta \frac{\delta \langle E \rangle}{\delta \gamma} + \sum_k \chi_k \frac{\delta \langle A_k \rangle}{\delta \gamma} \quad \text{case (b)}$$

(6)

As a result, the approximation provides the RCCE fundamental relation and its differential (RCCE Gibbs relation), respectively,

$$\dot{s} \approx \dot{s}(\gamma_{\text{RCCE}}(\ddot{e}, \ddot{n}, \ddot{a})) \quad \text{case (a)} \quad \quad \langle S \rangle_{\text{eq}} \approx \langle S \rangle(\gamma_{\text{RCCE}}(\langle E \rangle, \langle A \rangle)) \quad \text{case (b)}$$

(7)

$$\frac{d \gamma}{dt} = \gamma_{\text{RCCE}}(\gamma_{\text{eq}}) \quad \text{case (a)} \quad \quad \frac{d \gamma}{dt} = \gamma_{\text{RCCE}}(\gamma_{\text{eq}}) \quad \text{case (b)}$$

(8)

Where, of course, in case (a) $\beta = \partial \dot{s}(\gamma_{\text{RCCE}}(\ddot{e}, \ddot{n}, \ddot{a})) / \partial \ddot{e}, \lambda_i = \partial \dot{s}(\gamma_{\text{RCCE}}(\ddot{e}, \ddot{n}, \ddot{a})) / \partial \ddot{n}_i$, and $\chi_k = \partial \dot{s}(\gamma_{\text{RCCE}}(\ddot{e}, \ddot{n}, \ddot{a})) / \partial \ddot{a}_k$, and in case (b) $\beta = \partial \langle S \rangle(\gamma_{\text{RCCE}}(\langle E \rangle, \langle A \rangle)) / \partial \langle E \rangle$, and $\lambda_k = \partial \langle S \rangle(\gamma_{\text{RCCE}}(\langle E \rangle, \langle A \rangle)) / \partial \langle A_k \rangle$.

3 Unified formulation of basic nonequilibrium dynamical models

The explicit dependence of the entropy on the state variables $\gamma$ varies from model to model and in many frameworks it is a characteristic feature of the system. In Ref.\(^{[65]}\) we have shown that in spite of the differences in state variables, the essential elements of five broad frameworks of nonequilibrium modeling are based on dynamical laws with similar structure, of either of the two forms

$$\frac{\partial \gamma}{\partial t} + \nabla \cdot J^\gamma = \mathcal{R}_{\gamma,t} + \Pi_\gamma \quad \text{case (a)} \quad \quad \frac{d \gamma}{dt} = \mathcal{R}_{\gamma,t} + \Pi_\gamma \quad \text{case (b)}$$

(9)

where for case (a) the vector field $J^\gamma(x, t)$ denotes the vector of the fluxes of the components of the state vector field $\gamma$ — here, $J^\gamma = J^\beta + \gamma \nu$ where $J^\beta$ is the diffusive flux and $\nu$ the barycentric velocity of the fluid element, $\nu = J^\nu / \dot{m}$ where $J^\nu$ is the Lagrangian mass flux and $\dot{m}$ the fluid’s density — and $\Pi_\gamma(x, t)$ the dissipative contribution responsible for the local entropy production rate; and for both cases (a) and (b) — under the assumption that in spite of its interactions with external systems the system remains continuously well-separable (closed) and uncorrelated — the term $\mathcal{R}_{\gamma,t}$ includes both internal reversible contributions [such as the effects of chemical reactions in case (a) or of a time-independent Hamiltonian in case (b)] as well as the effects of interactions (such as models of work and heat interactions, and/or a time-dependent Hamiltonian) that produce exchanges of properties with external systems in case (b), whereas the term $\Pi_\gamma(x, t)$ accounts for the internal dissipative (entropy generating) contribution. In either form (a) or (b), the term $\Pi_\gamma$ is the only one responsible for entropy generation and it is incapable of altering the values of the conserved properties. We call $\Pi_\gamma$ the “dissipation component of the dynamics.”

The (Poisson, Hamiltonian) symplectic structure of the reversible term $\mathcal{R}_{\gamma,t}$ has been the subject of a large number of studies starting with \[75, 76\]. Starting with \[77, 78, 79\] for classical fields and \[82, 83, 81\] for
quantum thermodynamics, many have studied the (Riemannian, steepest entropy ascent) metric structure of the irreversible term $\Pi$. The resulting combined structure has been given different names depending on the fields of interest and points of view of the various authors. The main ones are: “metripectic structure” $\mathfrak{B}$ (see also $\mathfrak{B}$ and references therein), “GENERIC” (general equation for the nonequilibrium reversible-irreversible coupling $\mathfrak{B}$, see also $\mathfrak{B}$ for an explicit proof of its equivalence with SEA), “gradient flows,” “stochastic gradient flows,” and particle models, with “large deviation principles” providing strong links between them $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$.

As shown in $\mathfrak{B}$, the dynamical equation is of type (a) in several frameworks, including: rarefied gas dynamics and small-scale hydrodynamics $\mathfrak{B}$, rational extended thermodynamics, macroscopic nonequilibrium thermodynamics, and chemical kinetics $\mathfrak{B}$, mesoscopic nonequilibrium thermodynamics, and continuum mechanics with fluctuations $\mathfrak{B}$. It is of type (b) in several other frameworks, including: statistical or information-theoretic models of relaxation to equilibrium $\mathfrak{B}$, quantum statistical mechanics, quantum information theory, quantum thermodynamics, mesoscopic nonequilibrium quantum thermodynamics, hypo-equilibrium steepest entropy ascent quantum thermodynamics $\mathfrak{B}$, quantum mechanics, and chemical kinetics $\mathfrak{B}$, mesoscopic nonequilibrium thermodynamics, dynamics and small-scale hydrodynamics $\mathfrak{B}$, rational extended thermodynamics, macroscopic nonequilibrium quantum thermodynamics $\mathfrak{B}$.

For case (a), $J_{C_i} = \left( \frac{\delta \hat{c}_i}{\delta \gamma} \right) |_{\Pi_{\gamma}} = J_{C_i} + \hat{c}_i \mathbf{v}$ and, for any property $A$, the mass balance equation $\partial \rho / \partial t + \nabla \cdot \mathbf{J}_{A} = 0$ implies the Reynolds identity $\partial \rho / \partial t + \nabla \cdot \mathbf{J}_{A} = \hat{m} \mathbf{D}_{A} / \partial t + \nabla \cdot \mathbf{J}_{A}$ with $\mathbf{D}_{A} / \partial t = \hat{d} \mathbf{D}_{A} / \partial t + \hat{a} \mathbf{v}$. Under the local RCCE assumption (local equilibrium when all $\chi_k$‘s vanish) and local diffusion-type interaction between adjacent fluid elements ($J_{S} = \sum \mathbf{J}_{C_i} + \sum \mathbf{J}_{A_k}$), combining the balance equations for entropy, the charges, the RCCE constraints, and, for case (a), momentum, yields the expressions

$$
\Pi_{S} = \sum \mathbf{J}_{C_i} \cdot \nabla \beta_i + \sum \mathbf{J}_{A_k} \cdot \nabla \chi_k + \Phi + \sum \chi_k \Pi_{A_k} \quad \text{(a)} \quad \Pi_{S} = \sum \chi_k \Pi_{A_k} \quad \text{(b)}
$$

where $\Phi$ is the dissipation function (see $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$, $\mathfrak{B}$ and references therein for derivations including nonlocal effects), $\Pi_{A_k} = \left( \frac{\delta a_k}{\delta \gamma} \right) |_{\Pi_{\gamma}}$ in case (a) and $\Pi_{A_k} = \left( \frac{\delta (A_k)}{\delta \gamma} \right) |_{\Pi_{\gamma}}$ in case (b) denote the “dissipative production rates of the RCCE variables”, and similarly $\Pi_{S} = \left( \frac{\delta s}{\delta \gamma} \right) |_{\Pi_{\gamma}}$ in case (a) and $\Pi_{S} = \left( \frac{\delta (S)}{\delta \gamma} \right) |_{\Pi_{\gamma}}$ in case (b), denote the (local) entropy production rate.

4 «Fourth law of thermodynamics»: the dissipative component of evolution is in a direction of steepest entropy ascent (SEA)

We propose to call «fourth law of thermodynamics» a general modeling rule that captures a common essential feature of a wide range of models for the dynamical behaviour of systems far from equilibrium and, therefore, encompasses a large body of known experimental evidence. We propose to state it as a “steepest entropy ascent principle” as follows: For every state $\gamma$ of a system (close as well as far from equilibrium) the component of the law of time evolution (tangent vector) that is responsible for entropy generation (dissipation) is
Figura 4: Pictorial representation of steepest entropy ascent evolution for three materials with identical anisotropic entropy landscape (red elliptic contours), identical initial far-nonequilibrium state, but different conductivity tensors (here, for simplicity, assumed state independent): (Left) anisotropic (high horizontal conductivity); (Center) isotropic; (Right) anisotropic (high vertical conductivity). Each blue dashed ellipse (or circle, for the isotropic case) represents a local ball, i.e., the set of states that (with respect to the local metric) are all at some fixed small distance from the current nonequilibrium state. Among these states, the system chooses to evolve in the direction of the one that has maximal entropy.

The various nonequilibrium modeling approaches and levels of description differ in the bilinear metric operator field $G_\gamma$ (for shorthand we use the subscript $\gamma$ to denote that it is a function of the state) defined by the usual Riemannian expressions the length of a segment of a one-parameter curve $\gamma(t)$, such as $\ell(t_2,t_1) = \int_{t_1}^{t_2} \sqrt{(\gamma'(\gamma)G_{\gamma}^{-1})}\,dt$ and $(d\ell/dt)^2 = (\gamma'(\gamma)G_{\gamma}^{-1})$. As argued in Ref. [65] and discussed below in Section 5 for states near the stable equilibrium manifold the inverse $G^{-1}_\gamma$ of the metric operator $G_\gamma$ is directly related to the Onsager matrix of generalized conductivities.

Two systems $A$ and $B$ with identical kinematics, i.e., identical state spaces and the same conserved properties, may exhibit different nonequilibrium dynamics, i.e., starting from the same state $\gamma$ they evolve along different paths in state space if they are characterized by different local metric operators $G^A_\gamma \neq G^B_\gamma$. If instead also the local metric operators are equal, $G^A_\gamma = G^B_\gamma$, then they evolve along the same path but they may do so at different speeds if the intrinsic dissipation time fields are different, $\tau^A_\gamma \neq \tau^B_\gamma$. Figure 4 shows a pictorial representation of SEA evolutions from a far-nonequilibrium state towards stable equilibrium for three systems with the same anisotropic entropy landscape but different (state independent) metric tensors. To fix ideas this is the case of relaxation to equilibrium of an isolated composite material with microstructures that yield isotropic or anisotropic thermal conductivity.

The various nonequilibrium modeling approaches and levels of description differ in the bilinear metric forms adopted to define gradients and also in other fine geometrical and mathematical technicalities. The differences between SEA, GENERIC, and metriplectic structures are discussed in [87, Sec.IIIB], where we also prove in detail their essential equivalence. The metric that provides a SEA formulation of standard chemical kinetics is available since [102, Eq.(9)]. The Wasserstein metric operator makes “gradient flows” $\gamma(t)$ essentially steepest entropy ascent, when the generating functional is entropy(Lyapunov)-like, i.e., an $S$-function in the sense of [103]. The states $\gamma$ are points of a Riemannian manifold $(\mathcal{M},G)$ and there is an entropy-like (dimensionless) functional $\tilde{S}$ on $\mathcal{M}$. In dimensionless time $t = t/\tau$, the gradient flow of $\tilde{S}$ on $(\mathcal{M},G)$ is a dynamical system in $\mathcal{M}$ given by the differential equation $d\gamma/dt = \nabla S |_{\gamma}$. The metric operator $G$ is an essential element of the notion. It converts the differential $d\tilde{S}$ of $\tilde{S}$, which is a cotangent vector field, into the gradient of $\tilde{S}$, which is a tangent vector field: for all vector fields $v$ on $\mathcal{M}$, $(d\tilde{S}|v) = (\nabla \tilde{S}|G_\gamma|v)$. Therefore, for all vector fields $v$ along $\gamma$, $(d\tilde{S}|_{\gamma}|v) = (\nabla \tilde{S}|_{\gamma}|G_\gamma|v) = (d\gamma/dt|G_\gamma|v)$. The rate of change

\begin{align*}
\end{align*}
of the $\tilde{S}$ functional is $d\tilde{S}/d\tilde{t} = (\text{diff} \tilde{S}|_{\gamma} |d\gamma/d\tilde{t}|) = (d\gamma/d\tilde{t}|G_{\gamma}|d\gamma/d\tilde{t})$, exactly as in the SEA formulation. Moreover, as shown explicitly in [63, 83], any standard linear diffusion model, where for the diffusive fluxes one assumes $\mathbf{J}_{C_i} = D_{C_i} \cdot \nabla \beta_i$ and $\mathbf{J}_{A_k} = D_{A_k} \cdot \nabla \chi_k$ in terms of the local diffusion tensors $D_{C_i}$ and $D_{A_k}$, are steepest entropy ascent with respect to the (nontrivial) Wasserstein metric operator.

As derived in full details in [60, 65, 87], the SEA component of the evolution equation is given by

$$\Pi_{\gamma} = \frac{1}{\tau_{\gamma}} G_{\gamma}^{-1} \left( \frac{\delta \tilde{S}}{\delta \gamma} \right) \bigg|_C \quad \text{case (a)} \quad \Pi_{\gamma} = \frac{1}{\tau_{\gamma}} G_{\gamma}^{-1} \left( \frac{\delta(S)}{\delta \gamma} \right) \bigg|_C \quad \text{case (b)} \quad (13)$$

where $G_{\gamma}$ is the local metric operator (it takes and returns vectors on the local constant-charges leaf) and $\cdot|_C$ denotes the component of the variational derivative of the entropy tangent to the local constant-charge manifold, i.e., orthogonal to the variational derivatives of all the charges,

$$\frac{\delta \tilde{S}}{\delta \gamma} \bigg|_C = \frac{\delta \tilde{S}}{\delta \gamma} - \sum_i \beta_i(\gamma) \frac{\delta C_i}{\delta \gamma} \quad \text{case (a)} \quad \frac{\delta S}{\delta \gamma} \bigg|_C = \frac{\delta S}{\delta \gamma} - \sum_i \beta_i(\gamma) \frac{\delta (C_i)}{\delta \gamma} \quad \text{case (b)} \quad (14)$$

and the “nonequilibrium charge potentials” $\beta_i(\gamma)$ are defined at each state $\gamma$ by the solution of the system of equations expressing such orthogonality conditions, respectively, for the two cases

$$\left( \frac{\delta \tilde{S}}{\delta \gamma} \bigg|_C \right) = \sum_i \beta_i(\gamma) \left( \frac{\delta C_i}{\delta \gamma} \bigg|_C \right) \quad \text{(a)} \quad \left( \frac{\delta S}{\delta \gamma} \bigg|_C \right) = \sum_i \beta_i(\gamma) \left( \frac{\delta (C_i)}{\delta \gamma} \bigg|_C \right) \quad \text{(b)} \quad (15)$$

We have proved in the QT framework [93, 99, 103], and the result can be readily extended to all other frameworks, that among the equilibrium states only the maximum entropy one is not unstable (in the sense of Lyapunov, as specified in [103]). As a result, the maximum entropy states emerge as the only stable equilibrium ones in the sense of the Hatsopoulos-Keenan statement of the second law [23, 53]. In other words, an important part of the (Hatsopoulos-Keenan statement of the) second law emerges as a general theorem of the SEA evolution equation. In addition to meeting all the desiderata formulated in [103] for strong compatibility with thermodynamics and connecting a variety of important aspects of nonequilibrium, the SEA principle also implies an interesting set of time-energy and time-entropy uncertainty relations [106] that allow to estimate the lifetime of a nonequilibrium state without solving the equation of motion. Moreover, it allows a generalization of Onsager reciprocity to the far nonequilibrium [107] (the RCCE version is presented below).

Explicit forms of the combined Hamiltonian+SEA evolution equation assuming an isotropic (Fisher-Rao) metric ($G_{\gamma}$ the identity operator with $\gamma$ a square root of the density operator) is given in [81] for an isolated qubit, in [103] for a qubit interacting with a pump-probe laser field, and in [109] for a four-level qudit. For the isolated qubit Figure 5 shows the resulting trajectories inside the Bloch ball, on the $\langle X \rangle$-$\langle Y \rangle$-$\langle S \rangle$ constant-$\langle E \rangle$ surface, and on a $\langle E \rangle$-$\langle X \rangle$-$\langle S \rangle$ diagram. For applications of the SEA master equation in the framework of quantum computing protocols, see [110].

5 Far-non-equilibrium RCCE extension of Onsager reciprocity

As shown in [104, 65] in the QT framework, for states belonging to a constrained maximal entropy manifold, such as within the RCCE approximation, any SEA evolution equation (i.e., regardless of the particular form of the dissipative metric operator $G_{\gamma}$) entails a natural extension of Onsager’s reciprocity theorem beyond the near-equilibrium realm. In fact, when Eq. (9) holds for the functional derivative of the entropy, Eqs. (14) and (15) become, in terms of the “nonequilibrium constraint potentials” $\chi_k$ and the “projected functional derivatives of the constraints,”

$$\frac{\delta \tilde{S}}{\delta \gamma} \bigg|_C = \sum_k \chi_k \frac{\delta \tilde{A}_k}{\delta \gamma} \bigg|_C \quad \text{case (a)} \quad \frac{\delta(S)}{\delta \gamma} \bigg|_C = \sum_k \chi_k \frac{\delta (A_k)}{\delta \gamma} \bigg|_C \quad \text{case (b)} \quad (16)$$

$$\frac{\delta \tilde{A}_k}{\delta \gamma} \bigg|_C = \frac{\delta \tilde{A}_k}{\delta \gamma} - \sum_i \alpha_{ki}(\gamma) \frac{\delta C_i}{\delta \gamma} \bigg|_C \quad \text{(a)} \quad \frac{\delta (A_k)}{\delta \gamma} \bigg|_C = \frac{\delta (A_k)}{\delta \gamma} - \sum_i \alpha_{ki}(\gamma) \frac{\delta (C_i)}{\delta \gamma} \bigg|_C \quad \text{(b)} \quad (17)$$
Fig. 5: The states of an isolated qubit map one-to-one with the points of the Bloch ball: mixed states are inside, pure states are on the surface (Bloch sphere). A solution of the Hamiltonian+SEA(Fisher-Rao) dynamical equation is shown (red curves): (Left) on the \( (X)\)–\( (Y)\)–\( S\) constant energy surface; (Center) inside the Bloch ball; (Right) on the \( \langle E \rangle\)–\( (X)\)–\( S\) diagram. When the trajectory is projected onto the \( (E)\)–\( S\) plane, it is a straight constant-energy line approaching asymptotically maximal entropy for \( t \to \infty \) and zero entropy for \( t \to -\infty \). As shown in [81], for a state-independent intrinsic dissipation time \( \tau \), the rate of entropy production is given by \( \frac{dS}{dt} = -k_B \frac{r^2-\langle E \rangle^2}{r-\langle E \rangle} \left( \ln \frac{1+r}{1-r} \right)^2 \) where \( r = \sqrt{(X)^2 + (Y)^2 + \langle E \rangle^2} \), \( S = -k_B Tr \ln \rho = -\frac{1}{2} k_B \left[ (1+r) \ln(1+r) + (1-r) \ln(1-r) \right] \), and energy is relative to a point midway of the two energy levels and scaled by \( \hbar \Omega_\alpha \) (where \( \Omega_\alpha \) is the Larmor angular frequency), so that \( \langle E \rangle = \langle Z \rangle \).

where the “partial nonequilibrium constraint potentials” \( \alpha_k(\gamma) \) are defined by the solution, for each \( k \), of the system of equations expressing the orthogonality conditions

\[
\frac{\delta \bar{a}_k}{\delta \gamma} \frac{\delta \bar{c}_i}{\delta \gamma} = \sum_i \alpha_k(\gamma) \left( \frac{\delta \bar{c}_i}{\delta \gamma} \right) \quad \frac{\delta \langle A_k \rangle}{\delta \gamma} \frac{\delta \langle C_i \rangle}{\delta \gamma} = \sum_i \alpha_k(\gamma) \left( \frac{\delta \langle C_i \rangle}{\delta \gamma} \right)
\]

Thus, finally, by defining the “RCCE nonequilibrium Onsager generalized conductivities"

\[
L_{jk}(\gamma) = \frac{1}{\tau} \left( \frac{\delta \bar{a}_j}{\delta \gamma} \left| C \right| G_{\gamma}^{-1} \left| \frac{\delta \bar{a}_i}{\delta \gamma} \right| C \right) \quad L_{jk}(\gamma) = \frac{1}{\tau} \left( \frac{\delta \langle A_j \rangle}{\delta \gamma} \left| C \right| G_{\gamma}^{-1} \left| \frac{\delta \langle A_i \rangle}{\delta \gamma} \right| C \right)
\]

the SEA component of the evolution equation \([13]\) and the entropy production can be written as

\[
\Pi_\gamma = \frac{1}{\tau} \sum_k G_{\gamma}^{-1} \left( \chi_k \frac{\delta \bar{a}_k}{\delta \gamma} \right) \quad \Pi_\gamma = \frac{1}{\tau} \sum_k G_{\gamma}^{-1} \left( \chi_k \frac{\delta \langle A_k \rangle}{\delta \gamma} \right)
\]

\[
\Pi_S = \left( \frac{\delta \bar{S}}{\delta \gamma} \right| \Pi_\gamma \right) = \sum_j \sum_k \chi_j L_{jk}(\gamma) \chi_k \quad \Pi_S = \left( \frac{\delta \langle S \rangle}{\delta \gamma} \right| \Pi_\gamma \right) = \sum_j \sum_k \chi_j L_{jk}(\gamma) \chi_k
\]

The natural properties of symmetry and positive definiteness of the non-degenerate metric \( G_\gamma \) grant automatically (no additional assumptions needed) its invertibility (\( G_{\gamma}^{-1} \)) and the symmetry and non-negative definiteness of matrix \( L_{jk} \). In both cases we have

\[
\Pi_{Ak} = \sum_j \chi_j L_{jk}(\gamma)
\]

where we emphasize that the relations between rates \( \Pi_{Ak} \) and affinities \( \chi_k \) are nonlinear because the \( L_{jk} \)'s depend on \( \gamma \) which in turn (in the RCCE approximation) are nonlinear functions of the \( \chi_k \)'s. For a number of references and important comments on the history of internal variables (here, the \( \gamma \)'s) and variational formulations of non-equilibrium thermodynamics that lead to the quasi-linear structure of Eqs. \([21]\) and \([22]\), see \([101]\). Notice that here Eqs. \([19]\) provide explicit expressions for the \( L_{jk}(\gamma) \)'s in terms of the SEA metric \( G_\gamma \), the intrinsic dissipation time \( \tau_\gamma \), and the projected functional derivatives of the RCCE constraints.
Only in the near-equilibrium region we can approximate $L_{jk}(\gamma)$ with its stable-equilibrium value $L_{jk}(\gamma_{eq})$ and obtain the usual nonequilibrium linear rate-affinity relations and near-equilibrium Onsager reciprocity. For space limitations, we cannot pursue this further, but we will show elsewhere that most of the results and discussion presented in [73] for the case when the entropy is given by $-\sum_i p_i \ln p_i$ can be reformulated also in the present more general context.

We have shown in [107, 55] that Eqs. (19), which, again, provide explicit relations between the generalized far-nonequilibrium conductivities and the projected functional derivatives of the rate controlling constraints, have the form of a Gram matrix and represent a far-nonequilibrium generalization of the fluctuation-dissipation theorem.

6 Conclusion

Four general rules of thermodynamic modeling reveal four laws of Nature: (1) when the system is well separated from its environment, its energy must be defined for all states and must emerge as an additive, exchangeable, and conserved property; (2a) when the system is uncorrelated from any other system, its entropy must be defined for all states (equilibrium and nonequilibrium) and must emerge as an additive property, exchangeable with other systems as a result of temporary interactions, conserved in reversible processes and spontaneously generated in irreversible processes; (2b) for given values of the externally controllable parameters and of the conserved properties other than energy, the states that maximize entropy for a given value of the energy must be the only conditionally locally stable equilibrium points of the dynamical model (in the sense of [103 Def.8]); (3) among the stable equilibrium states, those with lowest energy must have zero temperature; (4) every nonequilibrium state of a system or local subsystem for which entropy is well-defined must be equipped with a metric in state space with respect to which the irreversible component of its time evolution is in the direction of steepest entropy ascent compatible with the conservation constraints.

Rules (1) to (3) are well-known essential features/consequences of the first, second, and third law of thermodynamics, respectively. Our main point in this paper is that an enormous body of scientific research devoted to modeling the essential features of nonequilibrium natural phenomena during the past four decades has converged from many different directions and frameworks towards the general recognition (albeit still expressed in different but equivalent forms and language) that also Rule (4) is indispensable. For this reason, we claim that it reveals a great law of Nature and, therefore, we propose to call it the fourth law of thermodynamics.

To illustrate the power of the proposed fourth law, we provide in Section 5 a new proof that, within the framework of the rate-controlled constrained-equilibrium (RCCE) approximation (also known as the quasi-equilibrium approximation), it allows to extend Onsager reciprocity and fluctuation-dissipation relations — which are well-known signatures of nonequilibrium dynamics in the near-equilibrium neighborhood — to the entire far-nonequilibrium state space, where the relations between affinities and dissipative rates (force-flux relations) are nonlinear, but have a quasi-linear structure.

The impressive revival of interest on thermodynamics over the past two decades has been fueled by the increasing roles that thermodynamics and quantum thermodynamics have started playing in a wide range of emerging and prospective technologies. Studies in these fields have evolved quite independently, and, for a long while, researchers from different fields (mechanical engineering, continuum mechanics, solid mechanics, physics, chemical engineering, nonequilibrium thermodynamics, quantum thermodynamics, mathematical physics) have developed their ideas often unaware of parallel developments ongoing or already done in other fields. Efforts like the present one to connect, distill, merge, and unify the essentials of these sparse contributions have already started, but it will take several years to fill completely the gap.

Many will argue that in some nonequilibrium frameworks steepest entropy ascent is an invalid or unnecessary principle. For example, a Referee insisted on the following remark (inserted here per explicit request of the Editor): «The "Steepest Entropy Ascent" may not be valid in Stochastic Thermodynamics where processes of negative entropy production exist. The conventional Non-Equilibrium Thermodynamics consisting of state space, balance equations, constitutive equations and Second Law, resulting in a system of differential equations solvable by taking constraints into account, does not need a steepest entropy ascent. May be that such a concept is hidden in the conventional procedure, but Stochastic Thermodynamics may be a counter-example."
In anticipation of discussions about the above remark, it is useful to keep in mind that: (1) the concept of “processes with negative entropy production” (see, e.g., [111]) has been already criticized (see, e.g., [112]); (2) in stochastic thermodynamic models of effects of strong system-bath correlations (such as echoes, recurrences, purity revivals), the microscopic definitions of internal energy, entropy, work, heat, free energy, available energy with respect to a thermal environment, adiabatic availability, etc. must satisfy strict consistency conditions (see, e.g., [45]); and (3) in such processes, the irreversible component of dynamics (potentially subject to the fourth law) is only the part of the evolution equation which is responsible for (fluctuating, but on average progressively) incomplete recurrences (see, e.g., [111, Fig.6] and [112, Fig.1]), due to lost or inaccessible correlations: for example, in kinetic theory, the collision integral in the highest order level of a truncated Bogoliubov-Born-Green-Kirkwood-Yvon (so-called BBGKY) hierarchy.

As John Maddox (perhaps the most famous editor of Nature) wrote 35 years ago (ten years before becoming an honorary fellow of the Royal Society) in an editorial about one of the earliest attempts to build a quantum thermodynamics [113], “this is a field in which the proof of the pudding is in the eating.”

Riferimenti bibliografici

[1] Feynman RP. 1964 The great conservation principles. In the Messenger Lectures series titled “The Character of Physical Law” given at Cornell University by Richard Feynman and recorded by BBC. London: BBC.

[2] Margenau H. 1950 The nature of physical reality: A philosophy of modern physics. New York, NY: McGraw Hill.

[3] Gyftopoulos EP, Beretta GP. 2005 Thermodynamics: Foundations and applications. Mineola, NY: Dover Publications.

[4] Hatsopoulos GN, Gyftopoulos EP. 1976 A unified quantum theory of mechanics and thermodynamics. Part IIa. Available energy. Found. Phys. 6 127–141. doi:10.1007/BF00708955

[5] Zanchini E, Beretta GP. 2014 Recent progress in the definition of thermodynamic entropy. Entropy 16 1547–1570. doi:10.3390/e16031547

[6] Beretta GP, Zanchini E. 2019 New definitions of thermodynamic temperature and entropy not based on the concepts of heat and thermal reservoir. Atti della Accademia Peloritana dei Pericolanti Classe di Scienze Fisiche Matematiche e Naturali. 97 (Suppl.1) A1. doi:10.1478/AAPP.97S1A1

[7] Öttinger HC. 1998 General projection operator formalism for the dynamics and thermodynamics of complex fluids. Phys. Rev. E 57 1416. doi:10.1103/PhysRevE.57.1416

[8] Grmela M. 2014 Contact geometry of mesoscopic thermodynamics and dynamics. Entropy 16 1652-1686. doi:10.3390/e16031652

[9] Pavelka M, Klíka V, Grmela M. 2014 Time reversal in nonequilibrium thermodynamics. Phys. Rev. E 90 062131. doi:10.1103/PhysRevE.90.062131

[10] Montefusco A, Peletier MA, Öttinger HC. 2018 Coarse-graining via the fluctuation-dissipation theorem and large-deviation theory. arXiv:1809.07253

[11] Chiavazzo E, Gorban AN, Karlin IV. 2007 Comparison of invariant manifolds for model reduction in chemical kinetics. Commun. Comput. Phys. 2 964–992.

[12] Lebiedz D, Reinhardt V, Siehr J. 2010 Minimal curvature trajectories: Riemannian geometry concepts for slow manifold computation in chemical kinetics. J. Comput. Phys. 229 6512–6533. doi:10.1016/j.jcp.2010.05.008

[13] Hiremath V, S. B. Pope SB. 2013 A study of the rate-controlled constrained-equilibrium dimension reduction method and its different implementations. Combust. Theory Model. 17 260–293. doi:10.1080/13647830.2012.752109
[14] Beretta GP, Rivadossi L, Janbozorgi M. 2018 Systematic constraint selection strategy for rate-controlled constrained-equilibrium modeling of complex nonequilibrium chemical kinetics. J. Non-Equilib. Thermodyn. 43 121–130. doi:10.1515/jnet-2017-0055

[15] Hatsopoulos GN, Gyftopoulos EP. 1976 A unified quantum theory of mechanics and thermodynamics. Part I. Postulates. Found. Phys. 6 15–31. doi:10.1007/BF00708660

[16] Hatsopoulos GN, Gyftopoulos EP. 1976 A unified quantum theory of mechanics and thermodynamics. Part IIb. Stable equilibrium states. Found. Phys. 6 439–455. doi:10.1007/BF00715033

[17] Hatsopoulos GN, Gyftopoulos EP. 1976 A unified quantum theory of mechanics and thermodynamics. Part III. Irreducible quantal dispersions. Found. Phys. 6 561–570. doi:10.1007/BF00715108

[18] Lieb EH, Yngvason J. 1999 The physics and mathematics of the second law of thermodynamics. Phys. Reps. 310 1–96. doi:10.1016/S0370-1573(98)00082-9

[19] Lieb EH, Yngvason J. 2013 The entropy concept for nonequilibrium states. Proc. Royal Society A 469 20139408. doi:10.1098/rspa.2013.0408

[20] Lieb EH, Yngvason J. 2014 Entropy meters and the entropy of non-extensive systems. Proc. Royal Society A 470 20140192. doi:10.1098/rspa.2014.0192

[21] Gyftopoulos EP, Beretta GP. 2015 What is the second law? ASME Journal of Energy Resources Technology 137 021003. doi:10.1115/1.4026379

[22] Brandao F, Horodecki M, Ng N, Oppenheim J, Wehner S. 2015 The second laws of quantum thermodynamics. PNAS 112 3275–3279. doi:10.1073/pnas.1411728112

[23] Weilenmann M, Krämer L, Faist P, Renner R. 2016 Axiomatic relation between thermodynamic and information-theoretic entropies. Phys. Rev. Lett. 117 260601. doi:10.1103/PhysRevLett.117.260601

[24] Hatsopoulos GN, Beretta GP. 2008 Where is the entropy challenge? AIP Conf. Proc. Series 1033 34–54. doi:10.1063/1.2979057

[25] Hatsopoulos GN, Keenan JH. 1965 Principles of general thermodynamics. New York: Wiley.

[26] Hatsopoulos GN, Gyftopoulos EP. 1979 Thermionic Energy Conversion, Vol. 2, Theory, Technology, and Application. Cambridge, MA: MIT Press.

[27] O’Connell JP, Haile JM. 2005 Thermodynamics: Fundamentals for applications. Cambridge University Press.

[28] Ebeling W, Sokolov IM. 2005 Statistical Thermodynamics and Stochastic Theory of Nonequilibrium Systems. Singapore: World Scientific.

[29] Lebon G, Jou D, Casas-Vázquez J. 2008 Understanding non-equilibrium thermodynamics. Foundations, applications, frontiers. (Vol. 295). Berlin: Springer.

[30] Kjelstrup S, Bedeaux D. 2008 Non-equilibrium thermodynamics of heterogeneous systems. Singapore: World Scientific.

[31] Beretta GP, Gyftopoulos EP. 2015 What is heat? ASME Journal of Energy Resources Technology 137 021006. [http://dx.doi.org/10.1115/1.4026382](http://dx.doi.org/10.1115/1.4026382)

[32] Weimer H, Henrich MJ, Rempp F, Schröder H, Mahler G. 2008 Local effective dynamics of quantum systems: A generalized approach to work and heat. EPL, Europhys. Lett. 83 30008. doi:10.1209/0295-5075/83/30008

[33] Levy A, Alicki R, Kosloff R. 2012 Quantum refrigerators and the third law of thermodynamics. Phys. Rev. E 85 061126. doi:10.1103/PhysRevE.85.061126
[34] Skrzypczyk P, Short AJ, Popescu S. 2014 Work extraction and thermodynamics for individual quantum systems. *Nature Commun.* **5** 4185. doi: 10.1038/ncomms5185

[35] Binder F, Vinjanampathy S, Modi K, Goold J. 2015 Quantum thermodynamics of general quantum processes. *Phys. Rev. E* **91** 032119. doi: 10.1103/PhysRevE.91.032119

[36] Esposito M, Ochoa MA, Galperin M. 2015 Nature of heat in strongly coupled open quantum systems. *Phys. Rev. B* **92** 235440. doi:10.1103/PhysRevB.92.235440

[37] Sparaciari C, Oppenheim J, Fritz T. 2017 Resource theory for work and heat. *Phys. Rev. A* **96** 052112. doi:10.1103/PhysRevA.96.052112

[38] Brandao FG, Horodecki M, Oppenheim J, Renes JM, Spekkens RW. 2013 Resource theory of quantum states out of thermal equilibrium. *Phys. Rev. A* **96** 052112.

[39] Yunger-Halpern N, Renes JM. 2016 Beyond heat baths: Generalized resource theories for small-scale thermodynamics. *Phys. Rev. E* **93** 022126. doi:10.1103/PhysRevE.93.022126

[40] Bender CM, Brody DC, Meister BK. 2002 Entropy and temperature of a quantum Carnot engine. *Proc. R. Soc. Lond. A* **458** 1519–1526. doi:10.1098/rspa.2001.0928

[41] Santos LF, Polkovnikov A, Rigol M. 2011 Entropy of isolated quantum systems after a quench. *Phys. Rev. Lett* **107** 040601. doi:10.1103/PhysRevLett.107.040601

[42] Beretta GP, Zanchini E. 2011 Rigorous and general definition of thermodynamic entropy in thermodynamics. In *Thermodynamics*. Tadashi M, Ed., Rijeka: InTechOpen, pp. 23–50. doi:10.5772/13371

[43] Beretta GP, Gyftopoulos EP. 2015 What is a simple system? *ASME Journal of Energy Resources Technology* **137** 021007. doi:10.1115/1.4026383

[44] Goldstein S, Huse DA, Lebowitz JL, Tumulka R. 2015 Thermal equilibrium of a macroscopic quantum system in a pure state. *Phys. Rev. Lett* **115** 100402. doi:10.1103/PhysRevLett.115.100402

[45] Jarzynski C. 2017 Stochastic and macroscopic thermodynamics of strongly coupled systems. *Phys. Rev. X* **7** 011008. doi:10.1103/PhysRevX.7.011008

[46] Zanchini E. 1986 On the definition of extensive property energy by the first postulate of thermodynamics. *Found. Phys.* **16** 923–935. doi:10.1007/BF00765339

[47] Zanchini E. 1988 Thermodynamics: energy of closed and open systems. *Il Nuovo Cimento B* **101** 453–465. doi:10.1007/BF00828923

[48] Zanchini E. 1992 Thermodynamics: energy of nonsimple systems and second postulate. *Il Nuovo Cimento B* **107** 123–139. doi:10.1007/BF02722911

[49] Kraus K. 1971 General state changes in quantum theory. *Ann. Phys.* **64** 311–335. doi:10.1016/0003-4916(71)90108-4

[50] Kossakowski A. 1972 On quantum statistical mechanics of non-Hamiltonian systems. *Rep. Math. Phys.* **3** 247–274. doi:10.1016/0034-4877(72)90010-9

[51] Ingarden RS, Kossakowski A. 1975 On the connection of nonequilibrium information thermodynamics with non-Hamiltonian quantum mechanics of open systems. *Ann. Phys.* **89** 451–485. doi:10.1016/0003-4916(75)90190-6

[52] Lindblad G. 1976 On the generators of quantum dynamical semigroups. *Commun. Math. Phys.* **119** 119–130. doi:10.1007/BF02172379

[53] Gorini V, Kossakowski A, Sudarshan ECG. 1976 Completely positive dynamical semigroups of N-level systems. *J. Math. Phys.* **17** 821–825. doi:10.1063/1.522979
[54] Spohn H. 1976 Approach to equilibrium for completely positive dynamical semigroups of N-level systems. *Rep. Math. Phys.* **10** 189–194. doi:10.1016/0034-4877(76)90040-9

[55] Beretta GP. 2010 Maximum entropy production rate in quantum thermodynamics. *J. Phys. Conf. Ser.* **237** 012004. doi:10.1088/1742-6596/237/1/012004

[56] Beretta GP. 2007 Well-behaved nonlinear evolution equation for steepest-entropy-ascent dissipative quantum dynamics. *Int. J. Quantum Inf.* **5** 249–255. doi:10.1142/S0219749907002700

[57] Cano-Andrade S, Beretta GP, von Spakovsky MR. 2015 Steepest-entropy-ascent quantum thermodynamic modeling of decoherence in two different microscopic composite systems. *Phys. Rev. A* **91** 013848. doi:10.1103/PhysRevA.91.013848

[58] Smith C. 2016 Comparing the models of steepest entropy ascent quantum thermodynamics, master equation and the difference equation for a simple quantum system interacting with reservoirs. *Entropy* **18** 176. doi:10.3390/e18050176

[59] Beretta GP, Gyftopoulos EP, Park JL. 1985 Quantum thermodynamics. A new equation of motion for a general quantum system. *Nuovo Cimento B* **87** 77–97.

[60] Beretta GP. 2009 Nonlinear quantum evolution equations to model irreversible adiabatic relaxation with maximal entropy production and other nonunitary processes. *Rep. Math. Phys.* **64** 139–168. doi:10.1016/S0034-4877(09)90024-6

[61] Gibbs JW. 1873 A method of geometrical representation of the thermodynamic properties by means of surfaces. *Transactions of Connecticut Academy of Arts and Sciences* **2** 382–404.

[62] Landau LD, Lifshitz EM. 1980 *Statistical Physics, Part I*. Elmsford, NY: Pergamon press.

[63] Mauri R. 2013 *Non-equilibrium thermodynamics in multiphase flows* New York, NY: Springer. doi:10.1007/978-94-007-5461-4

[64] Beretta GP, Gyftopoulos EP. 2015 What is the third law? *ASME Journal of Energy Resources Technology* **137** 021004. doi:10.1115/1.4026380

[65] Beretta GP. 2014 Steepest Entropy Ascent Model for Far-Non-Equilibrium Thermodynamics. Unified Implementation of the Maximum Entropy Production Principle. *Phys. Rev. E* **90** 042113. doi:10.1103/PhysRevE.90.042113

[66] Keck JC, Gillespie D. 1971 Rate-controlled partial-equilibrium method for treating reacting gas mixtures. *Combustion and Flame* **17** 237–241. doi:10.1016/S0010-2180(71)80166-9

[67] Keck JC. 1990 Rate-controlled constrained-equilibrium theory of chemical reactions in complex systems. *Progress in Energy and Combustion Science* **16** 125–154. doi:10.1016/0360-1285(90)90046-6

[68] Beretta GP, Keck JC, Janbozorgi M, Metghalchi H. 2012 The Rate-controlled constrained-equilibrium approach to far-from-local-equilibrium thermodynamics. *Entropy* **14** 92–130. doi:10.3390/e14020113

[69] Gorban AN, Karlin IV, Ilg P, Öttinger HC. 2001 Corrections and enhancements of quasi-equilibrium states *J. Non-Newtonian Fluid Mech.* **96** 203–219. doi:10.1016/S0377-0257(00)00135-X

[70] Kogan AM, Rozonoer LI. 1964 On the macroscopic description of kinetic processes (in russian). *Dokl. Akad. Nauk SSSR* **158** 566–569.

[71] Klika V, Pavelka M, Vágner P, Grmela M. 2019 Dynamic maximum entropy reduction *Entropy* **21** 715. doi:10.3390/e21070715

[72] Li G, von Spakovsky MR. 2016 Steepest-entropy-ascent quantum thermodynamic modeling of the relaxation process of isolated chemically reactive systems using density of states and the concept of hypoequilibrium state. *Phys. Rev. E* **93** 012137. doi:10.1103/PhysRevE.93.012137
[92] Mielke A, Peletier MA, Renger DRM. 2014 On the relation between gradient flows and the large-deviation principle, with applications to Markov chains and diffusion. *Potential Anal.* 41, 1293–1327. doi:10.1007/s11118-014-9418-5

[93] Reina C, Zimmer J. 2015 Entropy production and the geometry of dissipative evolution equations. *Phys. Rev. E* 92, 052117. doi:10.1103/PhysRevE.92.052117

[94] Embacher P, Dirr N, Zimmer J. 2018 Computing diffusivities from particle models out of equilibrium. *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 474(2212) 0694. doi:10.1098/rspla.2017.0694

[95] Yunger Halpern N, Faist P, Oppenheim J, Winter A. 2016 Microcanonical and resource-theoretic derivations of the thermal state of a quantum system with noncommuting charges. *Nat. Commun.* 7 12051. doi:10.1038/ncomms12051

[96] Beretta GP, Gyftopoulos EP, Park JL, Hatsopoulos GN. 1984 Quantum thermodynamics. A new equation of motion for a single constituent of matter. *Nuovo Cimento B* 82 169–191. doi:10.1007/BF02732871

[97] Gheorghiu-Svirschevski S. 2001 Nonlinear quantum evolution with maximal entropy production *Phys. Rev. A* 63 022105. doi:10.1103/PhysRevA.63.022105

[98] Gheorghiu-Svirschevski S. 2001 Addendum to “Nonlinear quantum evolution with maximal entropy production.” *Phys. Rev. A* 63 054102. doi:10.1103/PhysRevA.63.054102

[99] Antanovskii LK. 1996 Microscale theory of surface tension. *Phys. Rev. E* 54 6285. doi:10.1103/PhysRevE.54.6285

[100] Ván P. 2001 Weakly nonlocal irreversible thermodynamics—the Guyer–Krumhansl and the Cahn–Hilliard equations. *Phys. Lett. A* 290 88–92. doi:10.1016/S0375-9601(01)00657-0

[101] Ván P, Berezovski A, Engelbrecht J. 2008 Internal Variables and Dynamic Degrees of Freedom. *J. Non-Eq. Thermodynamics* 33 235–254. doi:10.1515/JNETDY.2008.010

[102] Sieniutycz S. 1987 From a least action principle to mass action law and extended affinity. *Chem. Eng. Sci.* 42, 2697–2711. doi:10.1016/0009-2509(87)87020-3

[103] Beretta GP. 1986 A theorem on Lyapunov stability for dynamical systems and a conjecture on a property of entropy *J. Math. Phys.* 27 305–308. doi:10.1063/1.527390

[104] Caticha A. 2001 Change, time and information geometry. *AIP Conf. Proc.* 568 72. doi:10.1063/1.1381872

[105] Beretta GP. 2005 Nonlinear extensions of Schroedinger-von Neumann quantum dynamics: A set of necessary conditions for compatibility with thermodynamics. *Mod. Phys. Lett. A* 20 977–984. doi:10.1142/S0217732305017263

[106] Beretta GP. 2019 Time–energy and time–entropy uncertainty relations in nonequilibrium quantum thermodynamics under steepest-entropy-ascent nonlinear master equations. *Entropy* 21 679. doi:10.3390/e21070679

[107] Beretta GP. 1987 Quantum thermodynamics of nonequilibrium. Onsager reciprocity and dispersion-dissipation relations. *Found. Phys.* 17 365–381. doi:10.1007/BF00733374

[108] Beretta GP. 1985 Effect of irreversible atomic relaxation on resonance fluorescence, absorption and stimulated emission. *Int. J. Theor. Phys.* 24 1233–1258. doi:10.1007/BF00670336

[109] Beretta GP. 2006 Nonlinear model dynamics for closed-system, constrained, maximal-entropy-generation relaxation by energy redistribution. *Phys. Rev. E* 73 026113. doi:10.1103/PhysRevE.73.026113
[110] Tabakin F. 2017 Model dynamics for quantum computing. *Ann. Phys.* **383** 33–78. doi:10.1016/j.aop.2017.04.013

[111] Bhattacharya S, Misra A, Mukhopadhyay C, Pati AK. 2017 Exact master equation for a spin interacting with a spin bath: Non-Markovianity and negative entropy production rate. *Phys. Rev. A* **95** 012122. doi:10.1103/PhysRevA.95.012122

[112] Esposito M, Lindenberg K, Van den Broeck C. 2010 Entropy production as correlation between system and reservoir. *New J. Phys.* **12** 013013. doi:10.1088/1367-2630/12/1/013013

[113] Maddox J. 1985 Uniting mechanics and statistics. *Nature* **316** 11. doi:10.1038/316011a0