NONLINEAR QUANTUM EVOLUTION EQUATIONS TO MODEL IRREVERSIBLE ADIABATIC RELAXATION WITH MAXIMAL ENTROPY PRODUCTION AND OTHER NONUNITARY PROCESSES

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We first discuss the geometrical construction and the main mathematical features of the maximum-entropy production/steepest-entropy-ascent nonlinear evolution equation proposed long time ago by this author in the framework of a fully quantum theory of irreversibility and thermodynamics for a single isolated or adiabatic particle, qubit, or qudit, and recently rediscovered by other authors. The nonlinear equation generates a dynamical group, not just a semigroup, providing a deterministic description of irreversible conservative relaxation towards equilibrium from any nonequilibrium density operator. It satisfies a very restrictive stability requirement equivalent to the Hatsopoulos–Keenan statement of the second law of thermodynamics. We then examine the form of the evolution equation we proposed to describe multipartite isolated or adiabatic systems. This hinges on novel nonlinear projections defining local operators that we interpret as "local perceptions" of the overall system's energy and entropy. Each component particle contributes an independent local tendency along the direction of steepest increase of the locally perceived entropy at constant locally perceived energy. It conserves both the locally perceived energies and the overall energy, and meets strong separability and nonsignaling conditions, even though the local evolutions are not independent of existing correlations. We finally show how the geometrical construction can readily lead to other thermodynamically relevant models, such as of the nonunitary isoentropic evolution needed for full extraction of a system's adiabatic availability.

Keywords: entropy, irreversibility, nonlinear quantum dynamics, steepest entropy ascent, maximum entropy production principle, quantum thermodynamics, Onsager reciprocal relations.

1. Introduction

In this paper, we construct a class of model evolution equations (applicable not only to open systems but also to closed isolated systems) capable of describing— simultaneously and in competition with the usual Hamiltonian unitary evolution—the natural tendency of any initial nonequilibrium state to relax towards canonical or partially-canonical thermodynamic equilibrium, i.e. capable of describing the irreversible tendency to evolve towards the highest entropy state compatible with the instantaneous mean values of the energy (and possibly other constants of the motion and other constraints).

In Introduction, we briefly review some essential challenges of a prevailing model of irreversibility (Section 1.1), we briefly discuss the original motivation that lead us to develop a quantum maximal entropy production formalism (Section 1.2), we discuss the geometrical framework of our derivation (Section 1.3), and we outline the structure of the rest of the paper (Section 1.4).

1.1. Kossakowski–Sudarshan–Gorini–Lindblad quantum master equation

The prevailing model of irreversibility starts from unitary dynamics but assumes that no system is truly isolated, so that even an initial pure state becomes mixed due to increasing system-environment entanglement.

The system-environment entanglement builds up due to interactions according to the standard Liouville–von Neumann unitary dynamics of the overall system-environment composite. In this phenomenological model a system A is assumed to be weakly coupled with a reservoir R, so that they can exchange energy via unitary evolution of the overall state ρ_{AR}. The reservoir R is modelled as a collection of a large number of quantum systems (many degrees of freedom, e.g. the modes of the electromagnetic field). Because of the weak coupling, the unitary dynamics of ρ_{AR} produces both an energy exchange and a build up of correlations between the system and the reservoir. However, justified only by some heuristic reasoning, a crucial *additional assumption* is injected in the derivation (Markovian approximation): that correlations *smear out* rapidly enough so as to maintain A and R *effectively* decorrelated not only initially, but at all times. One rationale usually offered for this approximation is that when the reduced density operator of A is time averaged (coarse grained) over a sufficiently long time interval, which is nevertheless still much shorter than the system's time scale of interest, the average correlations become negligible, and the averaged state effectively factors at all times. The model is phenomenological and basically charges the reservoir's complexity for the system's losing quickly its memory of past interactions.[1] By tracing out all the reservoir's degrees of freedom, the overall unitary dynamics gives rise (under such Markovian approximation) to a reduced system's dynamics which is nonunitary, linear, completely positive, and generated by the celebrated Kossakowski–Sudarshan–Gorini–Lindblad (KSGL) quantum master equation [5]

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2}\sum_j \left(2V_j^\dagger \rho V_j - \{V_j^\dagger V_j, \rho\}\right), \tag{1}$$

where the V_j's are some operators on $\mathcal{H}$ (each term within the summation, often written in the alternative form $[V_j, \rho V_j^\dagger] + [V_j\rho, V_j^\dagger]$, is obviously traceless). It has

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[1]The literature on the well-known problem of accounting for the arrow of time and the origin of irreversibility within statistical mechanics and its time reversible underlying dynamics is too vast to adequately review, see, e.g. [1]. Many alternatives to time averaging have been proposed as rationales for coarse graining (see e.g. [2–4]). We agree with a Referee, that a common feature of all these attempts to justify the continuing validity of the KSGL master equation, or equivalents, is that they require additional, question begging assumptions that are at odds with an overall unitary evolution.

been used for a number of successful models of dissipative quantum dynamics of open subsystems. Operators V_j in (1) are in general interpreted as creation and annihilation, or transition operators. For example, by choosing [6] $V_j = c_{rs}|r\rangle\langle s|$, where c_{rs} are complex scalars and $|s\rangle$ eigenvectors of the Hamiltonian operator H, and defining the transition probabilities $w_{rs} = c_{rs}c_{rs}^*$, the KSGL equation becomes

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\ \rho] + \sum_{rs} w_{rs}\left(|s\rangle\langle r|\rho|r\rangle\langle s| - \frac{1}{2}\{|s\rangle\langle s|,\rho\}\right), \qquad (2)$$

or, equivalently, for the nm-th matrix element of ρ in the H representation,

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar}\rho_{nm}(E_n - E_m) + \delta_{nm}\sum_r w_{nr}\rho_{rr} - \rho_{nm}\frac{1}{2}\sum_r (w_{rn} + w_{rm}), \qquad (3)$$

which, for the n-th energy level occupation probability $p_n = \rho_{nn}$, is the celebrated Pauli master equation

$$\frac{dp_n}{dt} = \sum_r w_{nr}p_r - p_n \sum_r w_{rn}. \qquad (4)$$

In this widely accepted model, the assumption of *erasure of correlations* is the sole mechanism responsible for "entropy generation" [7], but the apparent contradiction with the assumed underlying reversible unitary dynamics, i.e. the Loschmidt paradox is still lurking behind. The situation is parallel to what is needed to "derive" the classical Boltzmann equation from the underlying reversible Hamilton–Liouville dynamics.

Philosophically, we find it hard to understand how diffusion of mass, momentum, energy and charge, could find their justification in a "loss of *information* on the time scale of the observer leading to rapid decoherence from the entanglement which continuously builds up by weak coupling with environmental degrees of freedom". Is this the *real* physical reason for the "universal tendency in nature to the dissipation of mechanical energy" already recognized by Kelvin in 1852 [8]? Do we have alternatives to understand and model physical phenomena that are manifestly time asymmetric?

1.2. Locally maximal entropy production dynamics as a nonlinear alternative to the KSGL model equations

With this kind of motivation, thirty years ago we designed a possible alternative based on the assumption, still to be validated or invalidated, that irreversibility is a fundamental microscopic dynamical feature and as such it must be built into the fundamental laws of time evolution. Therefore, we constructed a fundamental nonunitary extension of standard Schrödinger unitary dynamics not contradicting any of the successful results of pure-state quantum mechanics, and yet entailing the second law as well as an objective entropy increase for mixed states of an isolated system. We have shown in [6, 9–12] that such an approach is possible based on a steepest-entropy ascent, i.e. maximal entropy generation, nonlinear and nonunitary

equation of motion which reduces to the Schrödinger equation for pure states. A 1985 *Nature* editorial [13] defined this approach "an adventurous scheme which may end arguments about the arrow of time". Until now, however, the theory has been rather ignored and neither validated nor invalidated experimentally. Therefore ("the proof of the pudding is in the eating" [13]), it remains just an interesting but little acknowledged and pursued theoretical alternative to the standard model. Some recent discussion about it, is found in [14]. The challenge with this approach is to ascertain if the intrinsic irreversibility it implies at the single particle (local, microscopic) level is experimentally verifiable, or else its mathematics must only be considered yet another phenomenological tool, at the same level as the quantum Markovian master equations which, as we have seen, are not free of their own challenges.

The central conceptual difference between the proposed approach, and the approaches based on attempting to derive the KSGL equation, is that this approach[2] regards a nonpure density matrix as representing a real ontological object, the actual state of the world, and is not understood as just an epistemic ignorance of which particular pure state the world is 'really' in.[3]

Therefore, we avoid the (unnecessary) severe restrictions imposed by linearity on the evolution equation, and we open up our attention to evolution equations nonlinear in the density operator ρ. It may at first appear natural to maintain the Kossakowski–Lindblad form (1) and simply assume that operators V_j are functions of ρ. This is true only in part for the evolution equation we will construct. Indeed, our hermitian operator ΔM in our Eq. (32) below, can always be written as $-\sum_j V_j^\dagger(\rho)V_j(\rho)$ and therefore our anticommutator term may be viewed as a generalization of the corresponding term in (1).

However, our geometrically motivated construction based on the square-root of the density operator effectively suppresses the term corresponding to $\sum_j V_j^\dagger \rho V_j$ in (1). The reason we find this suppression desirable is the following. Due to the terms $V_j^\dagger \rho V_j$ (1), whenever ρ is singular, its zero eigenvalues may change at a finite rate. This can be seen clearly from (4), by which dp_n/dt is finite whenever there is a nonzero transition probability w_{nr} from some other populated level ($p_r \neq 0$), regardless of whether p_n is zero or not. When this occurs, for one instant in time

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[2]To our knowledge, the first pioneering work where this assumption is made explicit and used consistently to build a unified quantum theory of mechanics and thermodynamics, is [15]. We thank a Referee for suggesting the wording of this paragraph and the following footnote.

[3]If one assumes that the 'true' state of the world is actually a pure state, and that the probabilities in a density matrix can only be a reflection of uncertainty, then it is fairly easy to see that the evolution of the density matrix must be linear: if $\rho_1 \to \rho_1'$ and $\rho_2 \to \rho_2'$, then a probabilistic mixture $p_1\rho_1 + p_2\rho_2 \to p_1\rho_1' + p_2\rho_2'$. This linearity does not need to hold for our proposed evolution law as a 'real' density matrix ρ is a distinct physical state, even though numerically it may be equal to $\rho = w_1\rho_1 + w_2\rho_2$ with $w_1 = p_1$ and $w_2 = p_2$, and is quite different from a probabilistic mixture arising through ignorance or uncertainty. Even if $\rho_1 \to \rho_1'$ and $\rho_2 \to \rho_2'$, it does not follow that $\rho = w_1\rho_1 + w_2\rho_2 \to w_1\rho_1' + w_2\rho_2'$. This conceptual difference is at the heart of our original approach. The physical reality attributed to the density matrix also legitimates treating the entropy $-k_B \text{Tr}(\rho \ln \rho)$ as a 'real' physical quantity, in the manner of energy or mass, and not as an expression of information or uncertainty about a probability distribution.

the rate of entropy change is infinite, as seen clearly from the expression of the rate of entropy change implied by (1),

$$\frac{d\langle S \rangle}{dt} = k_{\rm B} \sum_{j} {\rm Tr}(V_j^\dagger V_j \rho \ln \rho - V_j^\dagger \rho V_j \ln \rho) = k_{\rm B} \sum_{jrn}(V_j)_{nr}^{*}(V_j)_{nr}(\rho_r - \rho_n) \ln \rho_r, \quad (5)$$

where ρ_r denotes the r-th eigenvalue of ρ and $(V_j)_{nr}$ the matrix elements of V_j in the ρ representation.

We may argue that an infinite rate of entropy change can be tolerated, because it would last only for one instant in time. But the fact that zero eigenvalues of ρ in general would not remain zero (or close to zero) for longer than one instant in time, to us is an unphysical feature, at least because it is in contrast with a wealth of successful models of physical systems in which great simplification is achieved by limiting our attention to a restricted subset of relevant eigenstates (forming a subspace of $\mathcal{H}$ that we call the effective Hilbert space of the system [16]). Such common practice models yield extremely good results, which, being reproducible, ought to be relatively robust with respect to inclusion in the model of other less relevant eigenstates. In fact, such added eigenstates, when initially unpopulated, are irrelevant if they remain unpopulated (or very little populated) for long times, so that neglecting their existence should introduce very little error. The terms $V_j^\dagger \rho V_j$, instead, would rapidly populate such irrelevant unpopulated eigenstates and void the validity of our so successful simple models. Of course, we may deliberately overlook this instability problem by making highly ad-hoc assumptions, e.g. by forcing the V_j's to be such that $(V_j)_{nr} = 0$ whenever either $\rho_n = 0$ or $\rho_r = 0$. But, in this case, we can no longer claim true linearity with respect to ρ.

Another important general physical reason why we find it advantageous that our construction excludes KSGL terms that generate nonzero rates of change of the zero eigenvalues of ρ, is that such terms are construed so as to preserve the positivity of ρ in forward time, but in general they do not maintain it in backward time. Such mathematical irreversibility of the Cauchy problem is often accepted, presented, and justified as a natural counterpart of physical irreversibility. However, we already noted in [16] that it is more related to a principle of causality than to physical irreversibility. The strongest form of a general nonrelativistic principle of causality—a keystone of traditional physical thought—requires that future states of a system should unfold deterministically from initial states along smooth unique trajectories in the state domain, defined for all times, future as well as past. Accepting mathematical irreversibility of the model dynamics, would imply giving up such causality requirement. The foundational virtue of our dynamical group is in its very existence, which shows a simple conceivable alternative whereby we are not compelled to cope with such a major conceptual loss. Regardless of these important but highly controversial foundational implications, we have shown in [17] that our Eq. (32) can effectively describe relaxation within an isolated system, and yet it is mathematically reversible, in the sense that it features existence and uniqueness of well-defined solutions both in forward and backward time.

Eq. (32) describes physically irreversible time evolutions, in the sense that the physical property described by the entropy functional $-k_B\text{Tr}(\rho \ln \rho)$ is a strictly increasing function of time for all states except the very restricted set of equilibrium states and limit cycles defined by Eq. (43) below.

Similarly to our presentation of MEPP dynamics in a general probabilistic but nonquantal framework in [18, 19], in this paper we focus on the mathematical features and the potential phenomenological applications of a quantal MEPP dynamical equation. We emphasize that the formalism has an intrinsic mathematical validity *per se* as a mere phenomenological tool. This may be useful also for those who remain understandably skeptical about the cited adventurous scheme of our original attempt to unify mechanics and thermodynamics, whereby, again, we proposed a resolution of the long-standing dilemma about the arrow of time based on building the Hatsopoulos–Keenan statement of the second law directly into the dynamical postulate of quantum theory.

On the other hand, if proved valid at the fundamental level as envisioned in its original framework, our nonlinear dynamical law would imply the incompleteness of unitary pure-state zero-entropy quantum mechanics and the need to broaden it as suggested in [15, 20]. In such context, our microscopic dynamical theory might also be seen to accomplish the program sought for with limited success in the 1980's by the Prigogine school [21, 22], namely, to build a mathematical theory of microscopic irreversibility (the question: "*minimal* entropy production or *maximal* entropy production?" is an interesting one, and, at least mathematically, is clarified in [23, 24] where it is shown that *maximal entropy production in general*, implies *minimal* entropy production at some constrained stationary states).

1.3. Maximal entropy production path in a maximum entropy landscape

The determination of a density operator of maximum entropy subject to a set of linear constraints has applications in many areas of quantum physics, chemistry, information, and probability theories [25–29]. The maximum entropy density operator typically represents a thermodynamic equilibrium state or a constrained-equilibrium state of the system under study.

Having set aside the cited implications on conceptual and physical quantum foundations, this paper focuses on the geometrical construction of our MEPP nonlinear quantum master equation, presented as the mathematical generalization of the maximum entropy problem to the nonequilibrium domain, by discussing a general rate equation for the description of smooth constrained relaxation of arbitrary nonequilibrium density operators towards maximum entropy. The nonlinear rate equation keeps the constraints constant at their initial values and increases the entropy until an unstable or stable maximum-entropy equilibrium state is approached. The unstable equilibrium density operators are those with at least one zero eigenvalue and all others canonically distributed (see Eq. (43) below). The rate equation is also consistent with an Onsager reciprocity theorem interestingly extended to the entire nonequilibrium domain.

Geometrically, it has a clear representation in square-root density operator state space. Every trajectory unfolds along a path of steepest entropy ascent compatible with the constraints (constrained geodesics). For an isolated system, the constraints

represent constants of motion. For more general quantum thermodynamics modeling, such as for rate-controlled constrained equilibrium modeling of chemical kinetics [28, 29], the constraints may be assigned a specified time-dependence.

The well-known maximum entropy problem which sets our context (landscape, to use the terminology of nonlinear optimization) is that of seeking a density operator ρ whose entropy $S(\rho) = -k_B \text{Tr}\rho \ln \rho$ is maximal subject to given magnitudes $\langle A_k \rangle$ of one or more linear constraints $\text{Tr}\rho A_k = \langle A_k \rangle$ for $k = 0, 1, \ldots, n$ where A_k is the hermitian operator associated with the k-th constrained observable. We assume the first constraint to be the normalization condition, so that $A_0 = I$ and $\langle A_0 \rangle = 1$. Moreover, as suitable to model a canonical isolated system, below we will assume for simplicity a single nontrivial constrained observable, the energy, represented by the Hamiltonian operator $A_1 = H$.

The maximizing density operator ρ^* can be written as $\rho^* = \exp\left(-\sum_{k=1}^{n} \lambda_k A_k\right)/Q$ with $Q = \text{Tr}\exp\left(-\sum_{k=1}^{n} \lambda_k A_k\right)$ where the Lagrange multipliers λ_k are determined by the values $\langle A_k \rangle$ of the constraints.

In this landscape, we wish to consider the following general problem in the nonequilibrium domain. We seek a time-dependent density operator, namely, an operator function (one-parameter family) $\rho(t)$, whose zero eigenvalues remain zero at all times and whose entropy $S(\rho(t))$ is maximally increasing with time t, i.e.

$$\max \quad -k_B \frac{d}{dt}\text{Tr}\rho(t) \ln \rho(t) \geq 0 \quad \text{subject to} \quad \text{Tr}\rho(t)A_k = \text{const} \quad \text{and} \quad \frac{d\ell(t)}{dt} = \text{const},$$

(6)

where $\ell(t)$ is a properly formulated measure of length of a trajectory in density operator state space. In time interval dt, among all the possible trajectories in state space that have length $d\ell$, the system selects that which yields the maximal increase in the value of the entropy functional, i.e. the path of steepest entropy ascent. This models a most irreversible quantum evolution towards maximum entropy. It is a realization at the (fundamental?) quantum dynamical level of the "principle of maximal entropy generation" [30, 31]. The empirical validity of such a principle at the phenomenological level has been recently affirmed (explicitly or implicitly) by various authors in different fields and frameworks (see, e.g. [23, 32–36]).

Though overlooked even in recent reviews [36], our nonlinear dynamics is one of the earliest instances and implementations of the ansatz which today goes under the name of maximum entropy production principle (MEPP). A reason for the oversight may have been that starting in 1984 [30, 31] we classified our approach as 'steepest entropy ascent' dynamics, rather than MEPP, to emphasize that the qualifying and unifying feature of this dynamical principle is the direction of maximal entropy increase rather than the rate at which a nonequilibrium state is attracted in such direction.

The formalism presented here has mathematical features of great generality, and is presented in a form readily adaptable to different applications. It was originally "designed" by the author in 1981 [6] and subsequently developed [9, 10, 11, 17, 30, 31] to obtain an equation of motion for a quantum theoretical unification of mechanics and thermodynamics [13, 15].

Recently, the original equation has been partially rediscovered in the same context [37]. The idea of steepest-entropy-ascent time evolution of a probability distribution has also been recently rediscovered in [38] but with important differences we discuss in [17]. Because of its intriguing general features, we suggested long time ago [18] that the formalism maintains its appeal even when abstracted from its original physics purpose because it provides a powerful mathematical tool for phenomenological modeling applications. It has been recently rediscovered also in such a broader maximum entropy formalism, probabilistic context [39].

1.4. Outline of the paper

In Section 2 we present the geometrical reasoning that leads to the construction of our main equation, Eq. (32), for a single particle system. Important to this development (as well as the rest of the paper) is the material in Appendix, which reviews some well-known but little used geometrical notions, and sets the notation of our derivations.

In Section 3 we outline the main features and theorems of Eq. (32).

In Section 4 we discuss the generalization of our dynamics to composite systems, which is nontrivial in view of the nonlinearity of the steepest entropy approach.

Finally, in Section 5 we discuss a further generalization of the foregoing nonequilibrium problem whereby the magnitudes $\langle A_k \rangle$ of the constraints and the entropy rate of change may be assigned definite or interrelated time-dependences. This may become useful in the framework of quantum thermodynamics modeling of a non-work interaction, by which we mean [40] an interaction where in addition to energy exchange between the interacting systems, there is also entropy exchange.

2. Geometrical construction of a single-particle MEPP quantum dynamics

2.1. Reformulation in terms of square-root density operators

Because we seek a well-defined time evolution equation for the density operator, we must enforce at all times the positive semi-definiteness and hermiticity constraints, i.e. $\rho(t)^{\dagger} = \rho(t) \geq 0$. To this end it is convenient to change variables and represent quantum states by means of the square-root density operator γ defined as

$$\gamma = U\sqrt{\rho}, \qquad U^{\dagger} = U^{-1}, \qquad \rho = \gamma^{\dagger}\gamma, \tag{7}$$

where $\sqrt{\rho}$ is the positive square root of ρ, and U an arbitrary unitary operator that in the end will turn out to be irrelevant, much like phase factors in usual quantum mechanics. In the original derivations we assumed $U = I$, but as suggested in [37] the introduction of U has some formal advantage.

Notice that were it only to cope with the positive semi-definite constraint, we could choose as new 'variable' any function of ρ whose inverse is even. The main reason for choosing $\sqrt{\rho}$ is geometrical and part of the steepest entropy ascent assumption. We note here that, like done in [38] in a nonquantal context, we could derive a steepest entropy ascent dynamics without switching to a square root representation, but in such case the entropy gradient would not be well defined

on the entire domain, it would diverge whenever one of the eigenvalues of ρ is zero, and as a result the dynamics would exhibit unphysical infinite-rate effects and would not conserve positivity when solved backwards in time.

In order to introduce the geometrical notion of steepest entropy ascent, we need to define what we mean by "distance" between two density operators and by "length" of a portion of trajectory in state space, i.e. a one-parameter family of density operators, a time evolution. The proper unique natural metric for this purpose is known in statistics as the Fisher–Rao metric (see e.g. [41–43]). For a one-parameter family of discrete distributions, $\mathbf{p}(t)$, where t is the parameter, the distance between distributions $\mathbf{p}(t+dt)$ and $\mathbf{p}(t)$ is

$$
d\ell = \frac{1}{2}\sqrt{\sum_i p_i \left(\frac{d\ln p_i}{dt}\right)^2}\, dt = \frac{1}{2}\sqrt{\sum_i \frac{1}{p_i}\left(\frac{dp_i}{dt}\right)^2}\, dt = \sqrt{\sum_i \left(\frac{d\sqrt{p_i}}{dt}\right)^2}\, dt
$$

$$
= \sqrt{\sum_i (\dot{x}_i)^2}\, dt = \sqrt{\dot{\mathbf{x}} \cdot \dot{\mathbf{x}}}\, dt. \tag{8}
$$

Thus, square-root probabilities $x_i = \sqrt{p_i}$ are the most natural variables in that:
- the space becomes the unit sphere, $\mathbf{x} \cdot \mathbf{x} = 1$ ($\sum_i p_i = 1$);
- the Fisher–Rao metric simplifies to $d\ell = \sqrt{\dot{\mathbf{x}} \cdot \dot{\mathbf{x}}}\, dt$, or equivalently $d\ell^2 = d\mathbf{x}\cdot d\mathbf{x}$;
- the distance between any two distributions is the angle $d(\mathbf{x}_1, \mathbf{x}_2) = \cos^{-1}(\mathbf{x}_1 \cdot \mathbf{x}_2)$.

We therefore conveniently rewrite the density operator formalism in terms of the square-root-density operator representation of states. To do so, we equip the space of linear (not necessarily hermitian) operators on $\mathcal{H}$ with the *real* scalar product[4]

$$
X \cdot Y = \tfrac{1}{2}\,\mathrm{Tr}(X^\dagger Y + Y^\dagger X). \tag{9}
$$

The state space becomes the unit sphere $\gamma \cdot \gamma = 1$ ($= \mathrm{Tr}\rho$ with $\rho = \gamma^\dagger \gamma$ automatically positive semidefinite). On this state space, for convenience we adopt the Fisher–Rao type of metric $d(\gamma_1, \gamma_2) = \sqrt{2}\cos^{-1}(\gamma_1 \cdot \gamma_2)$, so that along a time dependent trajectory

$$
d\ell = 2\sqrt{\dot{\gamma} \cdot \dot{\gamma}}\, dt. \tag{10}
$$

2.2. Notation. gradients of the energy and entropy functionals

For simplicity, in addition to the normalization constraint, here we will assume a single additional constraint, namely, energy conservation,[5] with associated Hamiltonian H hermitian on $\mathcal{H}$. The extension to more constraints is straightforward [44]

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[4]Note that this *real* inner product on the vector space of linear operators does satisfy the necessary rules, including of course that $X \cdot Y = Y \cdot X$, $X \cdot X \geq 0$, and $X \cdot X = 0$ iff $X = 0$. It clearly differs from the more usual *complex* inner product $\mathrm{Tr}(X^\dagger Y)$.

[5]If H depends on a set of time dependent parameters $\lambda_1, \lambda_2, \ldots, \lambda_K$, the system is *adiabatic* and we usually interpret $\langle dH/dt \rangle = \sum_k \langle \partial H/\partial \lambda_k \rangle \dot{\lambda}_k$ as the rate of work exchange between the system and a set of K "work elements" [15] mechanically coupled with the system through the variation of these parameters. Such an adiabatic system undergoes what in [40] we call a "weight process", and the energy balance equation (energy conservation) reads $d\langle H \rangle/dt = \langle dH/dt \rangle$ or, in the notation we introduce in this section, $H' \cdot \dot{\gamma} = 0$.

in view of the formalism in Appendix. In terms of the square-root density operator γ, the functionals representing the mean values, their time rates of change along a time dependent trajectory $\gamma(t)$, and the dispersions and covariance of the energy and the entropy, are conveniently rewritten introducing the following notation[6,7]

$$H' = 2\gamma H, \qquad \text{so that } \mathrm{Tr}\rho H = \langle H \rangle = \tfrac{1}{2} H' \cdot \gamma; \tag{11}$$

$$S' = 2\gamma S, \qquad \text{with } S = -k_{\mathrm{B}} P_{\mathrm{Ran}\rho} \ln \rho = -k_{\mathrm{B}} \ln(\rho + P_{\mathrm{Ker}\rho}), \tag{12}$$

so that

$$\langle S \rangle = -k_{\mathrm{B}} \mathrm{Tr}\rho \ln \rho = \tfrac{1}{2} S' \cdot \gamma; \tag{13}$$

$$(\Delta H)' = 2\gamma \Delta H, \qquad \text{with } \Delta H = H - \langle H \rangle I, \text{ so that } (\Delta H)' \cdot \gamma = 0; \tag{14}$$

$$(\Delta S)' = 2\gamma \Delta S, \qquad \text{with } \Delta S = S - \langle S \rangle I, \text{ so that } (\Delta S)' \cdot \gamma = 0; \tag{15}$$

$$\dot{\rho} = \dot{\gamma}^\dagger \gamma + \gamma^\dagger \dot{\gamma}, \qquad \text{since } \rho = \gamma^\dagger \gamma; \tag{16}$$

$$\mathrm{Tr}\dot{\rho} = \dot{\gamma} \cdot \gamma + \gamma \cdot \dot{\gamma} = 2\gamma \cdot \dot{\gamma} = 0, \qquad \text{since } \mathrm{Tr}\rho = \gamma \cdot \gamma = 1; \tag{17}$$

$$d\langle H \rangle/dt - \langle dH/dt \rangle = \mathrm{Tr}\dot{\rho}H = \tfrac{1}{2}(\dot{\gamma} \cdot H' + \gamma \cdot \dot{H}') = H' \cdot \dot{\gamma}; \tag{18}$$

$$d\langle S \rangle/dt = d(-k_{\mathrm{B}}\mathrm{Tr}\rho \ln \rho)/dt = S' \cdot \dot{\gamma}; \tag{19}$$

$$\langle \Delta H \Delta H \rangle = \mathrm{Tr}\rho(\Delta H)^2 = \gamma \Delta H \cdot \gamma \Delta H = \tfrac{1}{4}(\Delta H)' \cdot (\Delta H)'; \tag{20}$$

$$\langle \Delta S \Delta S \rangle = \mathrm{Tr}\rho(\Delta S)^2 = \gamma \Delta S \cdot \gamma \Delta S = \tfrac{1}{4}(\Delta S)' \cdot (\Delta S)'; \tag{21}$$

$$\langle \Delta S \Delta H \rangle = \langle \Delta H \Delta S \rangle = \tfrac{1}{2}\mathrm{Tr}\{\Delta S, \Delta H\} = \gamma \Delta S \cdot \gamma \Delta H = \tfrac{1}{4}(\Delta S)' \cdot (\Delta H)'; \tag{22}$$

where $P_{\mathrm{Ran}\rho} = I - P_{\mathrm{Ker}\rho}$ is the projector onto the range of ρ (the subspace given by the eigenvectors of ρ with nonzero eigenvalues). Because of Eqs. (17), (18) and (19) we call the operators 2γ, H' and S' the normalization gradient, energy gradient, and entropy gradient operators, respectively. In the same sense, $(\Delta H)'$ and $(\Delta S)'$ are the gradients of the null functionals $\mathrm{Tr}\rho(\Delta H)'$ and $\mathrm{Tr}\rho(\Delta S)'$.

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[6]It hinges on the inner product defined by (9). The logic and some details are as follows. For any hermitian A, we define $A' = 2\gamma A$ so that $\langle A \rangle = \mathrm{Tr}(\rho A) = \tfrac{1}{2} A' \cdot \gamma$ (clearly, in general A' is not hermitian). When the $'$ operation is applied to $\Delta A = A - \langle A \rangle I$, we obtain $(\Delta A)' = 2\gamma \Delta A$ and, in general, $(\Delta A)' \cdot \gamma = 0$. Next, because $\rho = \gamma^\dagger \gamma$ and $\mathrm{Tr}\rho = \gamma \cdot \gamma = 1$, we have $\mathrm{Tr}\dot{\rho} = \dot{\gamma} \cdot \gamma + \gamma \cdot \dot{\gamma} = 2\gamma \cdot \dot{\gamma} = 0$, $\dot{\gamma}A \cdot \gamma = \gamma A \cdot \dot{\gamma}$ and, therefore, $\mathrm{Tr}(\dot{\rho}A) = \mathrm{Tr}[(\dot{\gamma}^\dagger \gamma + \gamma^\dagger \dot{\gamma})A] = \tfrac{1}{2}\mathrm{Tr}[\dot{\gamma}^\dagger(2\gamma A) + (2\gamma A)^\dagger \dot{\gamma}] = A' \cdot \dot{\gamma} = (\Delta A)' \cdot \dot{\gamma}$. In general, therefore, $d\langle A \rangle/dt - \langle dA/dt \rangle = \mathrm{Tr}(\dot{\rho}A) = A' \cdot \dot{\gamma}$. For a time independent Hamiltonian H, $d\langle H \rangle/dt = H' \cdot \dot{\gamma}$. Moreover, because $\mathrm{Tr}(\rho \dot{S}) = 0$ (proof in the next footnote), we have $d\langle S \rangle/dt = S' \cdot \dot{\gamma}$ in spite of $S = -k_{\mathrm{B}} P_{\mathrm{Ran}\rho} \ln \rho$ being time dependent. Finally, for any hermitian pair A and B, we have the identity $\gamma \Delta A \cdot \gamma \Delta B = \tfrac{1}{2}(\langle \Delta A \Delta B \rangle + \langle \Delta B \Delta A \rangle)$. Because $\langle \Delta A \Delta B \rangle - \langle \Delta B \Delta A \rangle = \mathrm{Tr}(\rho[A, B])$, in general $\langle \Delta A \Delta B \rangle \neq \langle \Delta B \Delta A \rangle$ unless A and B commute or one of them commutes with ρ.

[7]To show that $\mathrm{Tr}(\rho \dot{S}) = 0$, we let $B = P_{\mathrm{Ran}\rho}$ and use the identity $B\dot{B}B = 0$ which follows from $B^2 = B$, $\dot{B}B + B\dot{B} = \dot{B}$, $B\dot{B}B + B\dot{B} = B\dot{B}$. Let P_α be the one-dimensional projectors $|\alpha\rangle\langle\alpha|$ onto the eigenvectors of ρ with nonzero eigenvalues p_α (repeated if degenerate). Then, $P_\alpha P_\beta = \delta_{\alpha\beta} P_\alpha$, $B = \sum_\beta P_\beta$, $P_\alpha B = B P_\alpha = P_\alpha$, $\rho = \sum_\alpha P_\alpha p_\alpha$, $\mathrm{Tr}\rho = \sum_\alpha p_\alpha = 1$, $\sum_\alpha \dot{p}_\alpha = 0$, $S = -k_{\mathrm{B}} \sum_\beta P_\beta \ln p_\beta$, always well defined because the sum is restricted to the nonzero p_β's, $\dot{S} = -k_{\mathrm{B}} \sum_\beta P_\beta \dot{p}_\beta/p_\beta - k_{\mathrm{B}} \sum_\beta \dot{P}_\beta \ln p_\beta$, and finally $\mathrm{Tr}(\rho \dot{S}) = -k_{\mathrm{B}} \sum_\beta \dot{p}_\beta - k_{\mathrm{B}} \sum_\alpha \sum_\beta \mathrm{Tr}(P_\alpha \dot{P}_\beta)p_\alpha \ln p_\beta = -k_{\mathrm{B}} \sum_\alpha \mathrm{Tr}(P_\alpha \dot{P}_\alpha)p_\alpha \ln p_\alpha = 0$ because $\mathrm{Tr}(P_\alpha \dot{P}_\beta) = \delta_{\alpha\beta}\mathrm{Tr}(P_\alpha \dot{P}_\alpha)$ and $0 = \mathrm{Tr}(B\dot{B}BP_\alpha) = \mathrm{Tr}(B\dot{B}P_\alpha) = \mathrm{Tr}(P_\alpha \dot{B}) = \sum_\beta \mathrm{Tr}(P_\alpha \dot{P}_\beta) = \mathrm{Tr}(P_\alpha \dot{P}_\alpha)$.

It is noteworthy that a dual set of definitions may be constructed using $\tilde{\gamma} = \sqrt{\rho}U = \gamma^{\dagger}$, $\rho = \tilde{\gamma}\tilde{\gamma}^{\dagger}$, $\tilde{H}' = 2\tilde{\gamma}^{\dagger}H$, $d\langle H\rangle/dt - \langle dH/dt\rangle = \tilde{H}' \cdot \tilde{\gamma}^{\dagger}$, and so on, leading however to the same results.

So, thinking geometrically, $\gamma(t)$ is a parameterized path in the (square root) density matrix space and $\dot{\gamma}(t)$ gives the tangent vector to this path. If the hermitian operator A is not varying directly with time, $A'(t) \cdot \dot{\gamma}(t)$ gives the rate of change of its mean value $\langle A\rangle(t)$ as one follows the given path. To maximize the rate of change of the mean value, the tangent vector $\dot{\gamma}(t)$ should be parallel to $A'(t)$, whereas to hold the mean value constant, it should be perpendicular. From this follows the interpretation of 2γ, H' and S' as the normalization, energy, and entropy gradients, respectively. For a trajectory $\gamma(t)$ to conserve normalization and energy, the tangent vector $\dot{\gamma}(t)$ must be always perpendicular to γ and H'. This holds automatically for unitary evolutions, for which $\dot{\gamma}(t)$ is perpendicular also to S' (see Section 2.3). For a more general evolution, to maximize the generation of entropy, $\dot{\gamma}(t)$ should be parallel to S', but in general this is in conflict with the conservation of normalization and energy. So, in Section 2.4 we take $\dot{\gamma}(t)$ to be parallel to the component of S' perpendicular to both γ and H', i.e. in the direction of greatest entropy increase consistent with the constraints of normalization and energy conservation.

2.3. Hamiltonian evolution and time-energy uncertainty relations

Eqs. (17) and (18) imply that γ remains unit norm and $d\langle H\rangle/dt = \langle dH/dt\rangle$ (energy conservation)[8] when $\dot{\gamma}$ is orthogonal to both γ and the energy gradient vector H'.

This is the case for purely Hamiltonian evolution, whereby

$$\dot{\gamma}_H = i\gamma\Delta H/\hbar \quad \Rightarrow \quad \dot{\rho}_H = -i[H,\rho]/\hbar. \tag{23}$$

Note that $\dot{\gamma}_H$ is everywhere orthogonal also to S' and hence also the entropy is time invariant. It is actually so in a very special way, as each eigenvalue of ρ is time invariant under unitary evolution. Note also that, since $\gamma\Delta H \cdot \gamma\Delta H = \langle\Delta H\Delta H\rangle = \hbar^2\dot{\gamma}_H \cdot \dot{\gamma}_H$, the Fischer–Rao metric we have chosen $d\ell = 2\sqrt{\dot{\gamma}_H \cdot \dot{\gamma}_H}\,dt = dt/\tau_H$, defines an intrinsic Hamiltonian time τ_H such that

$$\langle\Delta H\Delta H\rangle\,\tau_H^2 = \hbar^2/4. \tag{24}$$

This can be interpreted as the shortest characteristic time of unitary evolution, because indeeed the standard (Mandelstam–Tamm–Messiah [45]) time-energy uncertainty relation can be stated as follows [44, 46],

$$\tau_{FH}^2 = \langle\Delta F\Delta F\rangle/|d\langle F\rangle/dt|^2 \geq \tau_H^2 \quad \Rightarrow \quad \langle\Delta H\Delta H\rangle\,\tau_{FH}^2 \geq \hbar^2/4, \tag{25}$$

where F is any hermitian operator and τ_{FH} is the characteristic time of change of its mean value $\langle F\rangle$ under Hamiltonian evolution. A well-known implication of (25) is that the mean value $\langle F\rangle$ of any observable cannot change at a rate exceeding $2\sqrt{\langle\Delta F\Delta F\rangle\langle\Delta H\Delta H\rangle}/\hbar$.

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[8]In particular, $\langle H\rangle$ is time invariant if H is time independent (isolated system).

2.4. Time evolution along the path of steepest entropy ascent

Instead of pure Hamiltonian evolution, let us assume

$$\dot{\gamma} = \dot{\gamma}_H + \dot{\gamma}_D, \tag{26}$$

with $\dot{\gamma}_D$ in the direction of steepest entropy ascent compatible with the constraints $\dot{\gamma}_D \cdot \gamma = 0$ (conservation of $\mathrm{Tr}\rho = 1$) and $\dot{\gamma}_D \cdot H' = 0$ (energy conservation). Thus, we assume $\dot{\gamma}_D$ orthogonal to γ and H'. As a result it also turns out to be orthogonal to $\dot{\gamma}_H$.

To identify the direction of steepest entropy ascent, we follow a simple geometrical construction based on the well-known but seldom used standard geometrical notions reviewed in Appendix, which from here on we give for granted. Let $L(\gamma, H')$ denote the real linear span of vectors γ and H'. Denote by S'_L the orthogonal projection of the entropy gradient vector S' onto L, and by $S'_{\perp L}$ its orthogonal complement, so that

$$S' = S'_L + S'_{\perp L}. \tag{27}$$

Assume for simplicity that γ and H' are linearly independent (the case in which they are not is easily covered as done in Appendix). Then, we may write

$$S'_{\perp L(\gamma, H')} = \frac{\begin{vmatrix} S' & \gamma & H' \\ S' \cdot \gamma & \gamma \cdot \gamma & H' \cdot \gamma \\ S' \cdot H' & \gamma \cdot H' & H' \cdot H' \end{vmatrix}}{\begin{vmatrix} \gamma \cdot \gamma & \gamma \cdot H' \\ \gamma \cdot H' & H' \cdot H' \end{vmatrix}} = \frac{\begin{vmatrix} (\Delta S)' & (\Delta H)' \\ (\Delta S)' \cdot (\Delta H)' & (\Delta H)' \cdot (\Delta H)' \end{vmatrix}}{(\Delta H)' \cdot (\Delta H)'} \tag{28}$$

$$= (\Delta S)' - \frac{(\Delta S)' \cdot (\Delta H)'}{(\Delta H)' \cdot (\Delta H)'} (\Delta H)' = (\Delta S)' - \frac{\langle \Delta S \Delta H \rangle}{\langle \Delta H \Delta H \rangle} (\Delta H)'. \tag{29}$$

Clearly, operator $S'_{\perp L}$ is the component of the entropy gradient operator S' orthogonal to both γ and H'. Using the above expression, it can be readily verified that $S'_{\perp L}$ is orthogonal also to $\dot{\gamma}_H$ (23). Moreover, $S'_{\perp L} \cdot S'_{\perp L} = \langle \Delta S \Delta S \rangle - \langle \Delta H \Delta S \rangle^2 / \langle \Delta H \Delta H \rangle$.

Therefore, we assume that $\dot{\gamma}_D$ is in the "direction" of $S'_{\perp L}$, and we let

$$\dot{\gamma}_D = \frac{1}{4\tau_D} \frac{S'_{\perp L(\gamma, H')}}{\sqrt{S'_{\perp L(\gamma, H')} \cdot S'_{\perp L(\gamma, H')}}}, \tag{30}$$

where τ_D is some positive constant or functional of ρ which we call the "intrinsic characteristic time of dissipation" also for the reasons to be further discussed below. As done in our original work, for simplicity of notation we also define the positive characteristic time functional

$$\tau = \tau_D \sqrt{S'_{\perp L(\gamma, H')} \cdot S'_{\perp L(\gamma, H')}} / k_{\mathrm{B}}, \tag{31}$$

where k_{B} is Boltzmann's constant.

2.5. Dynamical equation for the density operator of an isolated system

When "translated" in density operator formalism, our equation of motion (26) with $\dot\gamma_D$ given by (30) may be written in the following compact form

$$\dot\rho = -\frac{i}{\hbar}[H,\rho] + \frac{1}{2\tau_D\sqrt{\langle\Delta M\,\Delta M\rangle}}\{\Delta M,\rho\},\ \text{where}\ M=S-\frac{H}{\theta_H}\ \text{and}\ \theta_H=\frac{\langle\Delta H\,\Delta H\rangle}{\langle\Delta S\,\Delta H\rangle}. \tag{32}$$

Operator M, that we call the "nonequilibrium Massieu operator", is a nonlinear function of ρ not only through the logarithmic dependence in operator S but also through the nonlinear functional θ_H, which we may call "constant-energy nonequilibrium temperature", because it will smoothly approach the equilibrium temperature as the state will approach at constant energy the maximal entropy stable equilibrium state (see below). Notice also that any reference to the square root operator γ disappears, proving that its use is only auxiliary to the given geometrical construction, as it is auxiliary to the equivalent variational formulation given in [37] (see below). For this reason, the first formulation [6] avoided the explicit use of $\sqrt{\rho}$.

3. Features of the proposed dynamics for a single isolated particle

Detailed proofs of the general features of Eq. (32) that we outline in this section are given in [9–11, 44, 46].

3.1. Conservation of nonnegativity of the density operator

Eq. (32) generates a smooth continuous path in state space and maintains at zero any initially zero eigenvalue of ρ. As a result, no eigenvalue can cross zero and become negative, neither in the future nor in the past, thus assuring conservation of the nonnegativity of ρ both in forward and backward time.

3.2. Entropy generation rate

The rate of entropy change (more precisely, entropy "generation", since so far Eq. (32) is meant to be a model for an isolated or an adiabatic system) takes the following various explicit expressions

$$\frac{d\langle S\rangle}{dt} = \frac{d(-k_B\,\mathrm{Tr}\rho\ln\rho)}{dt} = \dot\gamma\cdot S' = \frac{1}{4k_B\tau}S'_{\perp L}\cdot S'_{\perp L} = 4k_B\tau\,\dot\gamma_D\cdot\dot\gamma_D \tag{33}$$

$$= \frac{1}{k_B\tau}\langle\Delta M\,\Delta M\rangle = \frac{1}{k_B\tau}\left(\langle\Delta S\,\Delta S\rangle - \frac{\langle\Delta H\,\Delta H\rangle}{\theta_H^2}\right) = \frac{1}{\tau_D}\sqrt{\langle\Delta M\,\Delta M\rangle}, \tag{34}$$

and is clearly positive semi-definite owing to the well-known positive semi-definiteness of Gram determinants (Appendix) and scalar product norms [see the last two of Eqs. (33)].

3.3. Characteristic times and time-entropy uncertainty relation

Because of the orthogonality between $\dot{\gamma}_D$ and $\dot{\gamma}_H$, if at one time $[H, \rho] = 0$ then $\rho(t)$ commutes with H at all times. For such particular, "purely dissipative" trajectories, the Fisher–Rao metric takes on the following interesting explicit expressions

$$d\ell = 2\sqrt{\dot{\gamma}_D \cdot \dot{\gamma}_D}\, dt = \sqrt{\frac{1}{k_B\tau}\frac{d\langle S\rangle}{dt}}\, dt = \frac{1}{k_B\tau}\frac{d\langle S\rangle}{d\ell}\, dt \qquad (35)$$

$$= \frac{\sqrt{\langle \Delta M \Delta M\rangle}}{k_B\tau}\, dt = \frac{1}{k_B\tau}\sqrt{\langle \Delta S \Delta S\rangle - \frac{\langle \Delta H \Delta H\rangle}{\theta_H^2}}\, dt = \frac{dt}{\tau_D}, \qquad (36)$$

where the last equality justifies our calling τ_D the natural "intrinsic dissipative time". The last of Eqs. (35) shows that the alternate characteristic time τ is directly related to the rate $d\ell/dt$ at which the state operator γ follows the steepest entropy ascent trajectory, modulated by the dimensionless entropy gradient $d(S/k_B)/d\ell$ along the trajectory,

$$\frac{1}{\tau} = \frac{d\ell/dt}{d(S/k_B)/d\ell}, \qquad (37)$$

so, we see that when time intervals are measured in units of the "local" (or instantaneous) value of τ and entropy in units of k_B, the "speed" along the steepest entropy ascent trajectory (geodesic) coincides with the local slope of the entropy surface along the trajectory,

$$\frac{d\ell}{dt/\tau} = \frac{d(S/k_B)}{d\ell}, \qquad (38)$$

which again justifies the interpretation of τ as an intrinsic dynamical time. Finally, we notice that $dS/d\ell$ equals half of the norm of the component of the entropy gradient operator S' orthogonal to the linear manifold $L(\gamma, H')$ defined by the gradients of the constraints (here, for simplicity, only normalization and energy conservation),

$$dS/d\ell = \tfrac{1}{2}\sqrt{S'_{\perp L(\gamma,H')} \cdot S'_{\perp L(\gamma,H')}}. \qquad (39)$$

A noteworthy result follows from Eq. (34) together with the general inequality $\langle \Delta S \Delta S\rangle \geq \langle \Delta M \Delta M\rangle$ (Appendix). By defining the characteristic time τ_S of the entropy generation, we find the following general time-entropy uncertainty relations

$$\tau_S^2 = \frac{\langle \Delta S \Delta S\rangle}{|d\langle S\rangle/dt|^2} \geq \frac{\langle \Delta M \Delta M\rangle}{|d\langle S\rangle/dt|^2} = \frac{(k_B\tau)^2}{\langle \Delta M \Delta M\rangle} = \tau_D^2 \quad \Rightarrow \quad \langle \Delta M \Delta M\rangle\, \tau_S^2 \geq (k_B\tau)^2$$
$$(40)$$

and also

$$\langle \Delta S \Delta S\rangle\, \tau_S^2 \geq (k_B\tau)^2, \qquad (41)$$

which imply that the rate of entropy generation cannot exceed the following bounds,

$$d\langle S\rangle/dt \leq \sqrt{\langle \Delta S \Delta S\rangle}/\tau_D \leq \langle \Delta S \Delta S\rangle/k_B\tau \ . \qquad (42)$$

3.4. Equilibrium states and limit cycles

From Eq. (33) we see that the rate of entropy generation is zero (and the evolution is Schrödinger–von Neumann) if and only if $\dot{\gamma}_D = 0$, i.e. when S' lies in $L(\gamma, H')$. Then, the density operator may be written as

$$\rho = \frac{B \exp(-H/k_{\mathrm{B}}T)B}{\mathrm{Tr}[B \exp(-H/k_{\mathrm{B}}T)B]}, \qquad \text{for some } B = B^2, \qquad (43)$$

where $T = \theta_H = \langle \Delta H \Delta H \rangle / \langle \Delta H \Delta S \rangle = \theta_S = \langle \Delta H \Delta S \rangle / \langle \Delta S \Delta S \rangle = \sqrt{\langle \Delta H \Delta H \rangle / \langle \Delta S \Delta S \rangle}$. We call these the "nondissipative states". Proofs of the above and following results are straightforward, and detailed in the original papers [9–11, 30].

Because $\dot{\gamma}_D = 0$, nondissipative states remain nondissipative at all times, $-\infty < t < \infty$. Therefore they obey unitary Hamiltonian evolution. If $[B, H] = 0$ they are equilibrium states. If $[B, H] \neq 0$ their unitary evolutions are limit cycles of the dynamics, and $B(t) = U(t)B(0)U^{-1}(t)$ with $U(t) = \exp(-itH/\hbar)$. Limit cycles can be mixed, if $\mathrm{Tr}\,B > 1$, or pure, if $\mathrm{Tr}\,B = 1$. The latter case coincides with the usual Schrödinger dynamics of standard quantum mechanics. Except for when $B = I$ (the identity operator) all these equilibrium states and limit cycles are unstable (according to Lyapunov).

3.5. Dynamical group, not a semi-group

As proved in the original papers and again in [17, 37], the solutions of our non-linear dynamical equation form a group, not a semi-group, of "trajectories" in density operator space. This is so because of a very important feature of the dynamics, namely, that along every trajectory the zero eigenvalues of ρ are invariant, the range of ρ and its cardinality $\mathrm{Tr}\,P_{\mathrm{Ran}\rho}$ are invariant. However, the nonzero eigenvalues of ρ get smoothly rearranged towards higher entropy distributions approaching partially canonical distributions of the form (43). Because positive eigenvalues of ρ remain positive at all times, it follows that every trajectory is unique and well defined not only in forward time but also backwards in time (an explicit proof of the uniqueness feature is given in [47] for a two level system, and is also discussed in general in [37]).

We therefore have a "strongly causal" group of dynamical evolutions, with inverse defined everywhere, unique trajectories through every state ρ, fully defined both forward and backward in time, thus allowing full reconstruction of the past from the present. It is an example of an *invertible* dynamics which nevertheless is fully compatible with all thermodynamics principles and in addition is largely irreversible in that in forward time and for a system which is isolated (or "adiabatic" in the sense that the Hamiltonian operator may be time dependent) entails and describes explicitly entropy generation along the direction of maximal increase.

A remark about invertibility is in order. An often encountered, misleading assertion is that to be "irreversible" a dynamical evolution must not have an inverse. To justify the theory of dynamical semi-groups, the misleading suggestion has often been made that noninvertibility is an indispensable feature for the description of

thermodynamic irreversibility, so that the equation of motion can be solved only forward in time, not backwards, and *causality* is thus retained only in a "weak form": future states can be predicted from the present state, but the past cannot be reconstructed from the present.

Our nonlinear dynamical group challenges this idea. The existence of thermodynamic irreversibility is not incompatible with causality in the strong sense: it does not necessarily forbid the possibility to reconstruct the past from the present. If $\rho(0)$ and $\rho(t)$ are the states at times 0 and t, they are related by the dynamical map $\rho(t) = \Lambda_t(\rho(0))$ through the solution of the equation of motion for the time interval from 0 to t with initial condition $\rho(0)$. If the inverse map exists, it points from the final state back to the initial state, $\rho(0) = \Lambda_t^{-1}(\rho(t))$, and there is a one-to-one correspondence between initial and final state. This is our case. It shows that existence of the inverse map does not rule out the possibility that the functional which represents thermodynamic entropy could be *nondecreasing in forward time*. In [17] we present some numerical solutions which exemplify how any given distribution of eigenvalues belongs to a unique smooth solution which among other features identifies (as $t \to -\infty$) a lowest-entropy (not necessarily zero-entropy) "ancestral" or "primordial" state.

3.6. Stability of equilibrium states and the second law of thermodynamics

Each partially canonical equilibrium density operator of the form (43) maximizes the entropy when restricted to the subset of density operators that share the same kernel. Such states are equilibrium (i.e. time invariant if H is time invariant), but are unstable whenever at least one eigenvalue of ρ is equal to zero. In fact, a minor perturbation which changes the zero eigenvalue to an arbitrarily small nonzero value, would proceed away towards a quite different equilibrium of higher entropy. Instead, any trajectory with no null eigenvalues, maintains such feature at all times (invariance of the cardinality of the set of eigenvalues), and approaches in forward time the unique, fully canonical, maximum-entropy density operator compatible with the initial values of the constraints (remember that for simplicity we are considering here only systems whose approach to equilibrium is constrained only by energy conservation and, of course, normalization).

Therefore, the only dynamically stable equilibrium states (again, stable according to Lyapunov) are those given by Eq. (43) with $B = I$. There is only one such canonical density operator for every value of the mean energy $\langle H \rangle$, which through $\mathrm{Tr} H\rho = \langle H \rangle$ fixes the temperature T in (43). Existence and uniqueness of stable equilibrium states for every value of the energy is the essence of the Hatsopoulos–Keenan statement of the second law of thermodynamics, which we may state as follows [15, 40, 48]: *Among all the states of a system that have a given value of the energy and are compatible with a given set of values of the amounts of constituents and the parameters of the Hamiltonian, there exists one and only one stable equilibrium state.* From this statement of the second law, the Kelvin–Planck, the Clausius, and the Carathéodory statements can all be shown to follow as logical

consequences (explicit proofs of this assertion can be found in [40, p. 64–65 (Kelvin–Planck), p. 133–136 (Clausius), and p. 121 (Carathéodory)]).

This statement of the second law brings out very clearly the apparent conflict between mechanics and thermodynamics, a contrast that for over a century has been perceived as paradoxical. In fact, within mechanics, classical or quantum, the following so-called *minimum energy principle* applies: *Among all the states of a system that are compatible with a given set of values of the amounts of constituents and the parameters of the Hamiltonian, there exists one and only one stable equilibrium state, that of minimal energy.* Comparing this assertion with the statement of the second law just reviewed, leads to a paradox if we insist that the two theories of Nature contemplate the same set of states. Indeed, for fixed amounts of constituents and parameters of the Hamiltonian, mechanics asserts the existence of a unique stable equilibrium state (that of minimal energy), whereas thermodynamics asserts the existence of infinite stable equilibrium states (one for every value the mean energy can take).

The paradox is removed if we admit that the "pure" states contemplated by quantum mechanics are only a subset of those contemplated by thermodynamics. This resolving assumption was very controversial when Hatsopoulos and Gyftopoulos first introduced it in [15]. However today—more as a byproduct of the more recent vast literature on quantum entanglement and quantum information than as a result of thermodynamic reasoning—an assumption to this effect is ever more often being included in the postulates of quantum theory (compare for example the postulates of quantum theory as stated, e.g. in the recent [49] with those stated in 1968 by Park and Margenau [50]). The discussions on the relations between this fundamental assumption and thermodynamics is flourishing in the physics literature (see [14, 51] and references therein). Unfortunately, pioneering contributions such as [15] are seldom acknowledged.

As mentioned in Introduction, the validity of the present steepest-entropy-ascent or maximal-entropy-generation mathematical formalism even outside of the original framework for which it was developed [13, 15, 9, 10] has been recognized and suggested by this author long time ago, not only for quantum dynamical phenomenological modeling [30] but also as a general tool for modeling relaxation and redistribution of nonequilibrium probability or other positive-valued distributions in a variety of fields [18, 19].

3.7. Variational formulation

In 2001, Gheorghiu-Svirschevski [37] re-derived Eq. (32) from a variational principle that in our notation is

$$\max \frac{d\langle S \rangle}{dt} \quad \text{subject to} \quad \frac{d\langle H \rangle}{dt} = 0, \quad \frac{d\mathrm{Tr}\rho}{dt} = 0, \quad \text{and } \dot{\gamma}_D \cdot \dot{\gamma}_D = c^2, \quad (44)$$

where the last constraint signifies that we maximize the rate of entropy generation at fixed norm of the operator $\dot{\gamma}_D$, hence we are free to vary only its direction

(c^2 is some real functional independent of $\dot{\gamma}_D$). Introducing Lagrange multipliers,

$$L = \dot{\gamma}_D \cdot S' - \lambda_1 \, \dot{\gamma}_D \cdot \gamma - \lambda_H \, \dot{\gamma}_D \cdot H' - \lambda_\tau \, \dot{\gamma}_D \cdot \dot{\gamma}_D, \qquad (45)$$

and maximizing L with respect to $\dot{\gamma}_D$ yields

$$S' - \lambda_1 \gamma - \lambda_H H' - 2\lambda_\tau \, \dot{\gamma}_D = 0, \qquad (46)$$

where the multipliers must be determined by substitution in the constraint equations. It is easy to verify that our expression of $\dot{\gamma}_D$ in Eqs. (28) and (30) yields the explicit solution of Eq. (46). Using (36) we see that with $c^2 = 1/4\tau_D^2$ we get exactly our quantum dynamical evolution equation.

3.8. Onsager reciprocal relations even far from equilibrium

Any nonequilibrium ρ can be written as

$$\rho = \frac{B \exp(-\sum_j f_j X_j) B}{\mathrm{Tr} B \exp(-\sum_j f_j X_j)}, \qquad (47)$$

where the set $\{I, X_j\}$ spans the real space of hermitian operators on $\mathcal{H}$, and $B = B^2$ is a projector (actually, $B = P_{\mathrm{Ran}\rho}$).[9] We may call the set $\{X_j\}$ a "quorum" of observables, because the measurement of their mean values $\{\langle X_j \rangle\}$ fully determines the density operator. The empirical determination of a quantum state has been recently called "quantum tomography". In an almost forgotten seminal series of papers in 1970–1971, Park and Band [52] devised elegant systematic rules to construct such a quorum of observables.

Given such a quorum, we can write

$$\langle X_j \rangle = \mathrm{Tr}(\rho X_j), \qquad \langle S \rangle = k_B f_0 + k_B \sum_j f_j \langle X_j \rangle, \qquad \text{and} \quad k_B f_j = \left. \frac{\partial \langle S \rangle}{\partial \langle X_j \rangle} \right|_{\langle X_{i \neq j} \rangle}, \qquad (48)$$

where $k_B f_j$ may be interpreted as the "generalized affinity" or force, conjugated with the observable associated with operator X_j.

Let us focus on the dissipative term in our equation of motion (32) and the rate of change it induces on the mean value $\langle X_j \rangle$ of each quorum observable. We call it the "dissipative (part of the) rate of change" of observable X_j,

$$\langle \dot{X}_j \rangle_D = \dot{\gamma}_D \cdot X_j', \qquad \text{with} \quad X_j' = 2\gamma X_j. \qquad (49)$$

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[9]To prove Eq. (47), let $P_{\mathrm{Ker}\rho}$ denote the projector onto the kernel of ρ, i.e. the eigenspace belonging to the zero eigenvalue (if ρ is nonsingular, $P_{\mathrm{Ker}\rho}$ projects onto the null vector of $\mathcal{H}$), and let $B(\mathcal{H})$ denote the real space of the hermitian operators on $\mathcal{H}$, equipped with the inner product $X \cdot Y = \mathrm{Tr}(XY)$ and let $\{I, X_j\}$ be a basis for $B(\mathcal{H})$. The (nonnegative definite) operator $-\ln(\rho + P_{\mathrm{Ker}\rho})$ is well defined for every ρ and, since it belongs to $B(\mathcal{H})$, we may write it as $-\ln(\rho + P_{\mathrm{Ker}\rho}) = f_0 I + \sum_j f_j X_j$. Therefore, $\rho + P_{\mathrm{Ker}\rho} = e^{-f_0} \exp(-\sum_j f_j X_j)$. Multiplying by $P_{\mathrm{Ran}\rho}$ and using the identities $P_{\mathrm{Ran}\rho} P_{\mathrm{Ker}\rho} = 0$ and $P_{\mathrm{Ran}\rho}\rho = \rho P_{\mathrm{Ran}\rho} = \rho$, we obtain $\rho = e^{-f_0} P_{\mathrm{Ran}\rho} \exp(-\sum_j f_j X_j)$. Finally, by imposing $\mathrm{Tr}\rho = 1$, we find $e^{f_0} = \mathrm{Tr}[P_{\mathrm{Ran}\rho} \exp(-\sum_j f_j X_j)]$.

From the expressions we derived for $\dot{\gamma}_D$ in our steepest entropy ascent dynamics, we find the following *linear* relations between dissipative rates and affinities

$$\langle \dot{X}_i \rangle_D = \sum_j f_j L_{ij}(\rho), \tag{50}$$

where the coefficients are *nonlinear* functionals of ρ which form a symmetric, positive semi-definite Gram matrix $[\{L_{ij}(\rho)\}]$, "generalized conductivity",

$$L_{ij}(\rho) = \frac{1}{\tau} \frac{\begin{vmatrix} \langle \Delta X_i \Delta X_j \rangle & \langle \Delta H \Delta X_j \rangle \\ \langle \Delta X_i \Delta H \rangle & \langle \Delta H \Delta H \rangle \end{vmatrix}}{\langle \Delta H \Delta H \rangle} = L_{ji}(\rho), \tag{51}$$

As a result, the entropy generation rate may be written as a quadratic form in the affinities

$$\frac{d\langle S \rangle}{dt} = k_B \sum_i \sum_j f_i f_j L_{ij}(\rho). \tag{52}$$

When $[\{L_{ij}(\rho)\}]$ is positive definite, we denote its inverse, "generalized resistance", by $[\{R_{ij}(\rho)\}]$,

$$f_j = \sum_i R_{ij}(\rho) \langle \dot{X}_i \rangle_D, \tag{53}$$

and the entropy generation rate may then be written also as a quadratic form in the dissipative rates

$$\frac{d\langle S \rangle}{dt} = k_B \sum_i \sum_j L_{ij}^{-1}(\rho) \langle \dot{X}_i \rangle_D \langle \dot{X}_j \rangle_D, \tag{54}$$

as well as a sum of the dissipative rates of change of the quorum observables each multiplied by its conjugated affinity

$$\frac{d\langle S \rangle}{dt} = k_B \sum_i f_i \langle \dot{X}_i \rangle_D. \tag{55}$$

Notice that the parametrization of density operators given by Eq. (47) in terms of the real variables f_j, implies that we can write the entropy as $\langle S \rangle = \langle S \rangle(f_1, \ldots, f_{N^2-1})$ in view of the fact that our dynamics conserves the cardinality of ρ (and hence $\mathrm{Tr} B$ is invariant).

3.9. Nonlinear master equation for energy level occupation probabilities

When written for the nm-th matrix element of ρ with respect to an eigenbasis $\{|\epsilon_j\rangle\}$ of H, Eq. (32) becomes

$$\frac{d\rho_{nm}}{dt} = -\frac{i}{\hbar} \rho_{nm}(E_n - E_m) + \frac{1}{k_B \tau} \sum_r u_{nr} u_{mr}^* p_r \left(\Delta s_r - \frac{\Delta e_n + \Delta e_m}{2\theta_H} \right), \tag{56}$$

where $u_{jk} = \langle \epsilon_j | \eta_k \rangle$, $\{|\eta_k\rangle\}$ is an eigenbasis of ρ, p_k's its eigenvalues, $\Delta s_k = s_k - \langle S \rangle$, $s_k = -k_B \ln p_k$ if $p_k \neq 0$, $s_k = 0$ if $p_k = 0$, e_j the eigenvalues of H, $\Delta e_j = e_j - \langle H \rangle$, and θ_H, k_B and τ as already defined above. From (56) we see that if at one instant of time $[H, \rho] = 0$ and we select a common eigenbasis, then $u_{jk} = \delta_{jk}$ and $d\rho_{nm}/dt = 0$ for $n \neq m$, which means that the condition $[H, \rho] = 0$ holds along the entire trajectory. In such special but nontrivial cases, the eigenvalues of ρ get redistributed according to the nonlinear master equation

$$\frac{dp_n}{dt} = \frac{1}{k_B \tau} p_n \left(\Delta s_n - \frac{\Delta e_n}{\theta_H} \right), \tag{57}$$

whose fundamental features are analyzed and numerically exemplified in [17], where we wrote it in the following equivalent form

$$\frac{dp_n}{dt} = -\frac{1}{\tau} [p_n \ln p_n + \alpha \, p_n + \beta \, e_n p_n], \tag{58}$$

with the nonlinear functionals α and β defined by

$$\alpha = \frac{\sum_i e_i p_i \sum_j e_j p_j \ln p_j - \sum_i p_i \ln p_i \sum_j e_j^2 p_j}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i \right)^2},$$

$$\beta = \frac{\sum_i p_i \ln p_i \sum_j e_j p_j - \sum_i e_i p_i \ln p_i}{\sum_i e_i^2 p_i - \left(\sum_i e_i p_i \right)^2}. \tag{59}$$

In the usual statistical mechanics framework, the eigenvalues of ρ when $[\rho, H] = 0$ are interpreted as "occupation probabilities", meaning that the system is to be thought of as in a particular, unknown, pure state; then these "probabilities" are understood as an expression of the uncertainty as of which pure state the system is actually "occupying". In our original framework, instead, the eigenvalues of ρ when $[\rho, H] = 0$ are interpreted as "degrees of energy load sharing" among the different modes (eigenvectors of H) with which the system can internally accommodate its mean energy. From this point of view, entropy measures an overall degree of sharing between the available and active modes (i.e. those with nonzero eigenvalues). Entropy generation measures therefore the rate at which the spontaneous internal dynamics redistributes energy among the available modes, to achieve maximal sharing.

4. Extension of Eq. (32) to composite systems

The nonlinear, dissipative term $\dot{\gamma}_D$ in Eq. (26) provides a strong coupling between the energy storage modes of the single-particle system, additional to the coupling entailed by the linear, unitary term $\dot{\gamma}_H$ through the structure of the particle's Hamiltonian operator H. Were we to apply Eq. (26) without modifications to a system composed of two particles A and B (or to a more complex composite system) the term $\dot{\gamma}_D$ would couple the subsystems and make them exchange energy even in the absence of an interaction term in the Hamiltonian H, thus violating

both separability and no-signaling criteria. Because of the nonlinearity which is intrinsic in the steepest entropy ascent construction, if the model equation of motion is to meet these criteria, for a composite system, the structure of the interactions and the internal constraints between subsystems must be described not only through the Hamiltonian operator, but also through the structure of the dynamical equation itself.[10]

Suppose Alice and Bob, A and B, are the two elementary subsystems of an adiabatic system. Each subsystem is a single particle. Alice and Bob may be

$$\text{interacting: } H \neq H_A \otimes I_B + I_A \otimes H_B;$$

$$\text{noninteracting: } H = H_A \otimes I_B + I_A \otimes H_B;$$

$$\text{correlated/entangled: } S(\rho) \neq S(\rho_A) \otimes I_B + I_A \otimes S(\rho_B);$$

$$\text{uncorrelated: } S(\rho) = S(\rho_A) \otimes I_B + I_A \otimes S(\rho_B);$$

where here $S(\rho)$ denotes as before the operator $-k_B P_{\text{Ran}\rho} \ln \rho$, ρ is the density operator of the overall system, and ρ_A, ρ_B the reduced local density operators.

Our construction [6, 10] was designed so as to obtain a dynamical system obeying the following separability and no-signaling criteria [16].

- For permanently noninteracting subsystems A and B, every trajectory passing through a state in which the subsystems are in independent states ($\rho = \rho_A \otimes \rho_B$, where $\rho_A = \text{Tr}_B \rho$ and $\rho_B = \text{Tr}_A \rho$) must proceed through independent states along the entire trajectory, i.e. when two uncorrelated systems do not interact with each other, each must evolve in time independently of the other.

- If at some instant of time two subsystems A and B, not necessarily noninteracting, are in independent states, then the instantaneous rates of change of the subsystem's entropies $-k_B \text{Tr}(\rho_A \ln \rho_A)$ and $-k_B \text{Tr}(\rho_B \ln \rho_B)$ must both be nondecreasing in time.

- Two noninteracting subsystems A and B initially in correlated and/or entangled states (possibly due to a previous interaction that has then been turned off) should in general proceed in time towards less correlated and entangled states (*impossibility of spontaneous creation of any kind of correlations*).

- When subsystems A and B are not interacting, even if they are in entangled or correlated states, it must be impossible that the time dependence of any

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[10]It is noteworthy that if the proposed nonlinear evolution law is supposed to be a fundamental law of nature (i.e. not just a phenomenological modeling tool), then one should specify criteria for dividing a system into its separate elementary constituents. A unitary Hamiltonian dynamics depends only on the Hamiltonian operator H, regardless of the level of description, i.e. of whether we reach the given H by considering as elementary constituents the individual atoms, or the individual electrons within an atom and the nucleus, or the nucleons, or quark and gluons, or the electron field and quark field, etc. For the given H and a given mean value $\langle H \rangle$ of the energy, also the unique stable equilibrium state, $\rho_{\langle H \rangle} = \exp(-\beta_{\langle H \rangle} H) / \text{Tr} \exp(-\beta_{\langle H \rangle} H)$, is independent of the level of description. But if the relaxation to stable equilibrium is described by our nonlinear law, then the dynamics depends strongly on the assumed level of description, because through a unique internal relaxation time for each elementary subsystem, this dynamics fully couples all the internal modes of the elementary subsystem in a local effort to follow a path of steepest ascent in the locally perceived value of the overall entropy (see below).

local observable of one subsystem be influenced by any feature of the time evolution of the other subsystem (*no-signaling condition*).

Notice that we do not request that existing entanglement and/or correlations between A and B established by past interactions should have no influence whatsoever on the time evolution of the local observables of either A or B. In particular, there is no physical reason to request (as is often done) that two different states ρ and ρ' such that $\rho'_A = \rho_A$ should evolve with identical local dynamics ($d\rho'_A/dt = d\rho_A/dt$) whenever A does not interact with B, even if entanglement and/or correlations in state ρ differ from those in state ρ'. Rather, we see no reasons why the two local evolutions could not be different until spontaneous decoherence (if any) will have fully erased memory of the entanglement and the correlations established by the past interactions now turned off. In fact, this may be a possible experimental scheme to detect spontaneous decoherence. In other words, we will not assume that the local evolutions be necessarily Markovian.

Compatibility with the predictions of quantum mechanics about the generation of entanglement between interacting subsystems that emerge through the Schrödinger–von Neumann term $-i[H, \rho]/\hbar$, requires that the dissipative term may entail spontaneous loss of entanglement and loss of correlations between subsystems, but should not be able to create them.

To this end, we devised [6, 10] a construction which hinges on the definitions of the following "locally perceived energy" and "locally perceived entropy" operators, as a result of which our composite dynamics implements the ansatz of "steepest locally perceived entropy ascent",

$$(\Delta H)^A = \mathrm{Tr}_B[(I_A \otimes \rho_B)\Delta H] \quad \text{and} \quad (\Delta H)^B = \mathrm{Tr}_A[(\rho_A \otimes I_B)\Delta H], \qquad (60)$$

$$(\Delta S)^A = \mathrm{Tr}_B[(I_A \otimes \rho_B)\Delta S] \quad \text{and} \quad (\Delta S)^B = \mathrm{Tr}_A[(\rho_A \otimes I_B)\Delta S]. \qquad (61)$$

A geometrical construction (details in [6, 10, 44]) analogous to that outlined in Section 2 for a single particle, leads us to a composite-system steepest-locally-perceived-entropy-ascent dynamics with the form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2k_B\tau_A}\{(\Delta M)^A, \rho_A\} \otimes \rho_B + \frac{1}{2k_B\tau_B}\rho_A \otimes \{(\Delta M)^B, \rho_B\}, \qquad (62)$$

where τ_A, τ_B are local characteristic times and, for $J = A, B$,

$$(\Delta M)^J = (\Delta S)^J - (\Delta H)^J/\theta_{HJ} \quad \text{with} \quad \theta_{HJ} = \langle(\Delta H)^J(\Delta H)^J\rangle/\langle(\Delta S)^J(\Delta H)^J\rangle. \qquad (63)$$

Each local dissipative term separately "conserves" the overall system's mean energy $\langle H \rangle = \mathrm{Tr}(\rho H)$. Each subsystem's contribution to the overall system's rate of entropy change is positive semidefinite

$$\frac{d\langle S \rangle}{dt} = \frac{1}{k_B\tau_A}\langle(\Delta M)^A(\Delta M)^A\rangle + \frac{1}{k_B\tau_B}\langle(\Delta M)^B(\Delta M)^B\rangle. \qquad (64)$$

If Alice and Bob interact, it is only the Hamiltonian term in the evolution equation which during the interaction builds up correlations. Once generated, these

correlations survive even after A and B separate, even if they loose touch completely. When that happens, A and B remain correlated but begin to evolve independently of one another. This is reflected in the local structure of our equation and in particular of operators $(\Delta S)^A$, $(\Delta S)^B$, $(\Delta H)^A$, $(\Delta H)^B$.

Despite the nonlinearity, the equation prevents no-signaling violations, in that it satisfies the following *strong separability* conditions. Namely, denoting by $\dot{\rho}_{AB}(\rho, H)$ the r.h.s. of the equation, it is easy to show that, for any ρ and any H_A, H_B,

$$\text{Tr}_B[\dot{\rho}_{AB}(\rho, H_A \otimes I_B + I_A \otimes H_B)] = f_A\left((\Delta S)^A, H_A\right), \qquad (65)$$

$$\text{Tr}_A[\dot{\rho}_{AB}(\rho, H_A \otimes I_B + I_A \otimes H_B)] = f_B\left((\Delta S)^B, H_B\right). \qquad (66)$$

Conditions (65) and (66), when restricted to uncorrelated states, $\rho = \rho_A \otimes \rho_B$, define the conditions of *weak separability*, which of course are a corollary of strong separability.

However, existing correlations do influence the local evolutions, which therefore are not Markovian in that they do not depend only on the respective local (reduced) states ρ_A and ρ_B.

5. Additional phenomenological modeling equations for the density operator of a coupled system

In this section, we return to the problem of describing the effective interaction between a system and a reservoir. But instead of starting from Hamiltonian dynamics and adopting suitable approximations so as to arrive at the KSGL equation as discussed in Section 1.1, we take a fully phenomenological approach. Using our geometrical construction, it is easy to "design" dynamical equations that exhibit dynamical features that we expect from typically thermodynamical energy balance and entropy balance considerations. So, we may obtain a variety of similar dynamical equations that, though perhaps not as fundamental, may nevertheless be very useful in the phenomenological description of nonequilibrium phenomena of nonisolated systems.

For example, recent major advances in micro- and nano-technological applications, often call for a detailed description of the time evolution of nonequilibrium states that are far from thermodynamic equilibrium and cannot be described by partially canonical entropy density operators. In such far nonequilibrium regime, the assumption of linearity underlying the standard theory of irreversible processes may be cease to hold. Yet we may need to describe the simultaneous energy and entropy exchange which occurs between our quantum system and, say, a thermal reservoir at temperature T_Q, whereby the ratio of the energy to the entropy exchanged is equal to T_Q.

Thus, we will consider additional terms of the form

$$\dot{\rho} = \cdots + \frac{1}{2\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \{\Delta G, \rho\}, \quad \text{with } G = S - \frac{H}{\theta}, \qquad (67)$$

where the dots represent other terms as in (32) or even in the KGSL Eq. (1), G is another "nonequilibrium Massieu operator" that depends on the choice of functional

θ (see below), and τ_G is the characteristic time of decrease of $\langle G \rangle$. For $\theta = \theta_H$, G coincides with operator M in Eq. (32). Notice that if θ is chosen to be a constant, then $\tau_G d\langle G \rangle / dt = -\sqrt{\langle \Delta G \Delta G \rangle} < 0$ except for $\gamma G' = 0$, that is, $\gamma S' = \gamma H'/\theta$ or $\langle \Delta H \Delta H \rangle = \theta^2 \langle \Delta S \Delta S \rangle$ which occurs only for states of the form (43) with $T = \theta$.

Eq. (67) generates energy and entropy rates of change according to

$$\frac{d\langle H \rangle}{dt} = \frac{\langle \Delta H \Delta H \rangle}{\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \left(\frac{1}{\theta_H} - \frac{1}{\theta} \right) \quad \text{and} \quad \frac{d\langle S \rangle}{dt} = \frac{\langle \Delta S \Delta S \rangle}{\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \left(1 - \frac{\theta_S}{\theta} \right),$$
(68)

where $\theta_H = \langle \Delta H \Delta H \rangle / \langle \Delta H \Delta S \rangle$ and $\theta_S = \langle \Delta H \Delta S \rangle / \langle \Delta S \Delta S \rangle$ as defined before. Note that in general $\theta_H \geq \theta_S$ with strict equality only at states of form (43), and $\theta_H \theta_S \geq 0$ which means they always have the same sign (that of $\langle \Delta H \Delta S \rangle$).

Alternatively, we may also consider equations of the form

$$\dot{\rho} = \cdots - \frac{1}{2\tau_F \sqrt{\langle \Delta F \Delta F \rangle}} \{ \Delta F, \rho \}, \quad \text{with} \quad F = H - \theta S,$$
(69)

where F is a "nonequilibrium Helmholtz free energy operator" that depends on the choice of functional θ. In this case

$$\frac{d\langle H \rangle}{dt} = -\frac{\langle \Delta H \Delta H \rangle}{\tau_F \sqrt{\langle \Delta F \Delta F \rangle}} \left(1 - \frac{\theta}{\theta_H} \right) \quad \text{and} \quad \frac{d\langle S \rangle}{dt} = -\frac{(\theta_S - \theta)\langle \Delta S \Delta S \rangle}{\tau_F \sqrt{\langle \Delta F \Delta F \rangle}}.$$
(70)

Eqs. (69) and (70) are related to (67) and (68) by the fact that $\langle \Delta F \Delta F \rangle / \langle \Delta G \Delta G \rangle = \langle \Delta H \Delta H \rangle / \langle \Delta S \Delta S \rangle = \theta_H \theta_S$.

5.1. Smooth isentropic extraction of the adiabatic availability

When a system is in a nonequilibrium state, we call "adiabatic availability" the largest amount of energy that can be extracted in the form of work without leaving any other effects external to the system and without changing the system's Hamiltonian operator.[11] It is given by $\langle \Psi \rangle = \langle H \rangle - \langle H \rangle_s$ where $\langle H \rangle = \mathrm{Tr}[H\rho]$ is the mean energy of the nonequilibrium state and $\langle H \rangle_s = \mathrm{Tr}[H\rho_s(H)]$ the mean energy of the unique stable equilibrium state $\rho_s(H) = \exp(-\beta_s H)/\mathrm{Tr}\exp(-\beta_s H)$ that has the same entropy as the given state ρ, i.e. such that $\langle S \rangle = \langle S \rangle_s$. As thoroughly discussed in [40] in general terms, and in [15, 53] in the quantum framework, the adiabatic availability cannot in general be completely extracted by means of a unitary evolution, owing to the fact that a unitary process cannot change the eigenvalues of ρ. Instead, a process is required that while maintaining the entropy invariant, smoothly modifies the eigenvalues of ρ until they become canonically distributed. At the end of this isentropic change of state, ρ has the form (43) with $B = I$.

Whereas finding a practical way to control and interact with the system's dynamics so as to extract its adiabatic availability from an arbitrary initial state may be a very hard problem, our geometrical construction makes it straightforward to

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[11]Even if the Hamiltonian operator is a function $H(\lambda)$ of some controllable parameters, so that the state of the system is given by (ρ, λ), the adiabatic availability is the largest work that can be extracted with no net changes in λ.

design a dynamical equation that describes phenomenologically such an extraction, along a steepest-energy-descent trajectory at constant entropy. It suffices to take $\dot{\gamma}$ proportional to $-H'_{\perp L(\gamma, S')}$, i.e. the component the energy gradient H' orthogonal to both γ and S',

$$H'_{\perp L(\gamma, S')} = \frac{\begin{vmatrix} (\Delta H)' & (\Delta S)' \\ (\Delta H)' \cdot (\Delta S)' & (\Delta S)' \cdot (\Delta S)' \end{vmatrix}}{(\Delta S)' \cdot (\Delta S)'} = (\Delta H)' - \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle} (\Delta S)'. \quad (71)$$

In terms of Eq. (69) for the density operator, we may describe this by choosing

$$\theta = \theta_S = \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle}, \qquad F = F_\Psi = H - \theta_S S \qquad \text{and} \qquad \tau_F = \tau_{F_\Psi}, \quad (72)$$

therefore we may call θ_S the "constant-entropy nonequilibrium temperature" and F_Ψ the "constant-entropy nonequilibrium Helmholtz free energy operator". With this choice of θ in Eq. (69), the entropy remains constant while θ_S and θ_H smoothly approach the temperature of a canonical or partially canonical final state of lowest energy for the given entropy. Notice that the rate of energy change $d\langle H \rangle / dt$ is negative semidefinite (even for states with negative θ_H). Because the zero eigenvalues are time invariant here like for Eq. (32), this term will extract the full adiabatic availability only if the initial ρ in nonsingular.

5.2. Smooth extraction of the available energy with respect to a reservoir

When a system is in a nonequilibrium state or in any state not of mutual equilibrium with a given reservoir with temperature T_R, we call "available energy with respect to a reservoir with temperature T_R" the largest amount of energy that can be extracted in the form of work without any other effects external to the combination of the system and the reservoir. It is given by $\langle \Omega^R \rangle = \langle H \rangle - \langle H \rangle_R - T_R (\langle S \rangle - \langle S \rangle_R)$ where $\langle H \rangle_R$ and $\langle S \rangle_R$ are the energy and the entropy of the unique stable equilibrium state $\rho_R = \exp(-H/k_B T_R) / \mathrm{Tr} \exp(-H/k_B T_R)$ with temperature T_R. Again, its definition is discussed in [40] in general terms, and in [15] in the quantum framework.

We can design a dynamical equation that generates a trajectory along a smooth descent in available energy by taking Eq. (69) with

$$\theta = T_R, \qquad F = F_{\Omega^R} = H - T_R S \qquad \text{and} \qquad \tau_F = \tau_{F_{\Omega^R}}, \quad (73)$$

where T_R is the constant temperature of the reservoir and F_{Ω^R} is yet another "nonequilibrium Helmholtz free energy". With this choice of θ, the signs of the energy and entropy rates (70) depend on those of $1 - T_R / \theta_R$ and $\theta_S - T_R$. This is a model of a reversible weight process for the system-reservoir composite [40] where, by the energy and entropy balance equations, $T_R d\langle S \rangle / dt$ and $d\langle S \rangle / dt$ equal respectively the net rates of energy and entropy exchange (from the reservoir to the system, if positive, from the system to the reservoir, if negative). Therefore, the remaining power, $-d\langle H \rangle / dt + T_R d\langle S \rangle / dt = -d\langle \Omega^R \rangle / dt$, is the rate of energy

extraction in the form of work. From Eqs. (70) we see that the energy and entropy rates are both zero only at state ρ_R, where $\theta_H = \theta_S = T_R$.

5.3. Nonequilibrium heat interaction

As a final example, we consider the model of an interaction between our system in a nonequilibrium state ρ and some reservoir (heat bath) at T_Q, whereby the ratio of the energy and the entropy exchange rates is equal to T_Q. The usual definition of a heat interaction at T_Q (see [40] for a rigorous definition) requires both interacting bodies to be in states very close to their respective stable equilibrium states with temperature T_Q, because only then the ratio of energy to entropy exchanged is equal to T_Q. Therefore, the interaction we are modeling here is an extension of the standard notion to when one of the interacting systems is far from thermodynamic equilibrium (where temperature is not defined). It is easy to verify that by taking Eq. (69) with

$$\theta = \theta_Q = \theta_S \frac{\theta_H - T_Q}{\theta_S - T_Q}, \qquad F = F_{T_Q} = H - \theta_Q S \qquad \text{and} \qquad \tau_F = \tau_{F_{T_Q}}, \qquad (74)$$

we obtain a smooth trajectory where at all times $d\langle H\rangle/dt = T_Q\, d\langle S\rangle/dt$.

6. Conclusions

In this paper we discuss the geometrical construction and the main mathematical features of the maximum-entropy-production/steepest-entropy-ascent nonlinear evolution equation proposed long ago by this author in the framework of a fully quantum theory of irreversibility and thermodynamics for a single isolated or adiabatic particle, qubit, or qudit. The same mathematics has been recently rediscovered by other authors, with various physical interpretations.

The nonlinear equation generates a dynamical group, not just a semigroup like for KSGL dynamics. It provides a deterministic description of irreversible conservative relaxation towards equilibrium from an arbitrary initial density operator. It satisfies a very restrictive stability requirement equivalent to the Hatsopoulos-Keenan statement of the second law of thermodynamics which therefore emerges as a general theorem of the dynamics. It has smooth unique solutions both forward and backwards in time. Except for fully characterized families of limit cycles and of equilibrium states the entropy functional is strictly increasing in forward time and strictly decreasing in backward time. Viewed as a model of the relaxation to equilibrium of an isolated single particle system, this dynamics entails thermodynamic irreversibility at the single particle level.

For a multipartite isolated or adiabatic system, we introduce a nonlinear projection defining local operators that we interpret as "local perceptions" of the overall system's energy and entropy. Each component particle contributes an independent local tendency along the direction of steepest increase of the locally perceived entropy at constant locally perceived energy. It conserves both the locally-perceived energies

and the overall energy, and meets strong separability and nonsignaling conditions, even though the local evolutions are not independent of existing correlations.

In addition, we also show how the geometrical construction can readily lead to a variety of thermodynamically relevant models, such as the phenomenological descriptions of nonunitary isoentropic evolutions achieving full extraction of a system's adiabatic availability or available energy with respect to a reservoir, or the phenomenological descriptions of a nonunitary nonequilibrium heat interaction.

Acknowledgements

Appendix. Orthogonal decomposition of a vector with respect to a linear manifold

In the paper, we make extensive use of the notation and relations discussed in this appendix (see [18, 19] for a general but nonquantal context).

Given a set of vectors $\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n$, the symbol

$$L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n) \tag{75}$$

will denote their linear span, i.e. the linear manifold containing all the vectors that are (real) linear combinations of $\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n$. Given another vector $\mathbf{b}$, the symbol

$$\mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} \tag{76}$$

will denote the orthogonal projection of $\mathbf{b}$ onto the linear manifold $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$, namely, the unique vector in $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$ such that its dot product with any other vector $\mathbf{g}$ in $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$ equals the dot product of $\mathbf{b}$ with $\mathbf{g}$, i.e.

$$\mathbf{g} \cdot \mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} = \mathbf{g} \cdot \mathbf{b} \tag{77}$$

for every $\mathbf{g}$ in $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$.

In terms of a set of linearly independent vectors $\mathbf{h}_1, \ldots, \mathbf{h}_r$ spanning the manifold $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$, where clearly $r \leq n$, we can write two equivalent explicit expressions for the projection $(\mathbf{b})_{L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)}$ of vector $\mathbf{b}$ onto $L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)$. The first is

$$\mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} = \sum_{k=1}^{r} \sum_{m=1}^{r} (\mathbf{b} \cdot \mathbf{h}_k) \left[M(\mathbf{h}_1, \ldots, \mathbf{h}_r)^{-1} \right]_{k\,m} \mathbf{h}_m, \tag{78}$$

where $M(\mathbf{h}_1, \ldots, \mathbf{h}_r)^{-1}$ is the inverse of the Gram matrix

$$M(\mathbf{h}_1, \ldots, \mathbf{h}_r) = \begin{bmatrix} \mathbf{h}_1 \cdot \mathbf{h}_1 & \cdots & \mathbf{h}_r \cdot \mathbf{h}_1 \\ \vdots & \ddots & \vdots \\ \mathbf{h}_1 \cdot \mathbf{h}_r & \cdots & \mathbf{h}_r \cdot \mathbf{h}_r \end{bmatrix}. \tag{79}$$

The second expression is a ratio of two determinants

$$
\mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} = -\frac{\begin{vmatrix} 0 & \mathbf{h}_1 & \cdots & \mathbf{h}_r \\ \mathbf{b}\cdot\mathbf{h}_1 & \mathbf{h}_1\cdot\mathbf{h}_1 & \cdots & \mathbf{h}_r\cdot\mathbf{h}_1 \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{b}\cdot\mathbf{h}_r & \mathbf{h}_1\cdot\mathbf{h}_r & \cdots & \mathbf{h}_r\cdot\mathbf{h}_r \end{vmatrix}}{\begin{vmatrix} \mathbf{h}_1\cdot\mathbf{h}_1 & \cdots & \mathbf{h}_r\cdot\mathbf{h}_1 \\ \vdots & \ddots & \vdots \\ \mathbf{h}_1\cdot\mathbf{h}_r & \cdots & \mathbf{h}_r\cdot\mathbf{h}_r \end{vmatrix}}, \tag{80}
$$

where the determinant at the denominator, also given by $\det M\,(\mathbf{h}_1, \dots, \mathbf{h}_r)$, is always strictly positive because the vectors $\mathbf{h}_1, \dots, \mathbf{h}_r$ are linearly independent.

In the paper, our rate equations are expressed in terms of vectors of the form

$$
\mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} = \mathbf{b} - \mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} = \frac{\begin{vmatrix} \mathbf{b} & \mathbf{h}_1 & \cdots & \mathbf{h}_r \\ \mathbf{b}\cdot\mathbf{h}_1 & \mathbf{h}_1\cdot\mathbf{h}_1 & \cdots & \mathbf{h}_r\cdot\mathbf{h}_1 \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{b}\cdot\mathbf{h}_r & \mathbf{h}_1\cdot\mathbf{h}_r & \cdots & \mathbf{h}_r\cdot\mathbf{h}_r \end{vmatrix}}{\begin{vmatrix} \mathbf{h}_1\cdot\mathbf{h}_1 & \cdots & \mathbf{h}_r\cdot\mathbf{h}_1 \\ \vdots & \ddots & \vdots \\ \mathbf{h}_1\cdot\mathbf{h}_r & \cdots & \mathbf{h}_r\cdot\mathbf{h}_r \end{vmatrix}}, \tag{81}
$$

where in writing Eq. (81) we make use of Eq. (80). The vector $\mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)}$ is orthogonal to manifold $L\,(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)$; indeed, the vector represented by Eq. (81) has the relevant property

$$
\mathbf{g}_k \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} = 0, \qquad k = 0, 1, \dots, n, \tag{82}
$$

which follows directly from (77), and hence the relation

$$
\mathbf{b} = \mathbf{b}_{L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} + \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} \tag{83}
$$

represents the unique orthogonal decomposition of vector $\mathbf{b}$ with respect to the manifold $L\,(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)$.

Moreover, we have the other obvious, but relevant properties

$$
\mathbf{b} \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} = \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)} \geq 0, \tag{84}
$$

where the strict inequality applies whenever $\mathbf{b}$ is not in $L\,(\mathbf{g}_0, \mathbf{g}_1, \dots, \mathbf{g}_n)$, and for

any $\mathbf{a}$ and $\mathbf{b}$

$$\mathbf{a} \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} = \mathbf{a}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} \geq 0. \tag{85}$$

An important formula which derives from Eq. (81) and the usual properties of determinants, is

$$\mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} \cdot \mathbf{b}_{\perp L(\mathbf{g}_0, \mathbf{g}_1, \ldots, \mathbf{g}_n)} = \frac{\det M(\mathbf{b}, \mathbf{h}_1, \ldots, \mathbf{h}_r)}{\det M(\mathbf{h}_1, \ldots, \mathbf{h}_r)}. \tag{86}$$

Moreover, choosing the set of linearly independent vectors $\mathbf{h}_1, \ldots, \mathbf{h}_r$ so that $\mathbf{h}_r = 2\gamma$ is the gradient of the normalization constraint ($\mathrm{Tr}\rho = \gamma \cdot \mathbf{h}_r/2$), and defining the "mean" functionals $\langle H_j \rangle = \mathrm{Tr}\rho H_j = \mathbf{h}_j \cdot \mathbf{h}_r/4$ [in the paper, we assume $r = 2$, with $H_1 = H$, the Hamiltonian operator, and $H_2 = I$ the identity, so that $\mathbf{h}_1 = H' = 2\gamma H$ and $\langle H_1 \rangle = \mathrm{Tr}\rho H = \gamma \cdot H'/2 = (2\gamma) \cdot (2\gamma H)/4 = \mathbf{h}_1 \cdot \mathbf{h}_2/4$], $\langle B \rangle = \mathbf{b} \cdot \mathbf{h}_r/4$ [in the paper, $B = S$, $\mathbf{b} = S'$], and the "deviation" vectors $\Delta \mathbf{h}_j = (\mathbf{h}_j - \mathbf{h}_r \langle H_j \rangle)/2$, $\Delta \mathbf{b} = (\mathbf{b} - \mathbf{h}_r \langle B \rangle)/2$, it is easy to show that

$$\frac{\det M(\mathbf{b}, \mathbf{h}_1, \ldots, \mathbf{h}_n)}{\det M(\mathbf{h}_1, \ldots, \mathbf{h}_n)} = \frac{\det M(\Delta \mathbf{b}, \Delta \mathbf{h}_1, \ldots, \Delta \mathbf{h}_{n-1})}{\det M(\Delta \mathbf{h}_1, \ldots, \Delta \mathbf{h}_{n-1})}. \tag{87}$$

As a final remark, we write the following generalized form of the Cauchy–Schwarz inequality

$$\det M(\Delta \mathbf{b}, \Delta \mathbf{h}_1, \ldots, \Delta \mathbf{h}_{n-1}) \leq \det M(\Delta \mathbf{h}_1, \ldots, \Delta \mathbf{h}_{n-1}) \, \Delta \mathbf{b} \cdot \Delta \mathbf{b}. \tag{88}$$

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