

Maximum entropy production rate in quantum thermodynamics

Gian Paolo Beretta

Università di Brescia, via Branze 38, 25123 Brescia, Italy

E-mail: beretta@ing.unibs.it

Abstract. In the framework of the recent quest for well-behaved nonlinear extensions of the traditional Schrödinger–von Neumann unitary dynamics that could provide fundamental explanations of recent experimental evidence of loss of quantum coherence at the microscopic level, a recent paper [Gheorghiu-Svirschevski 2001 *Phys. Rev. A* **63** 054102] repropose the nonlinear equation of motion proposed by the present author [see Beretta G P 1987 *Found. Phys.* **17** 365 and references therein] for quantum (thermo)dynamics of a single isolated indivisible constituent system, such as a single particle, qubit, qudit, spin or atomic system, or a Bose-Einstein or Fermi-Dirac field. As already proved, such nonlinear dynamics entails a fundamental unifying microscopic proof and extension of Onsager’s reciprocity and Callen’s fluctuation–dissipation relations to all nonequilibrium states, close and far from thermodynamic equilibrium. In this paper we propose a brief but self-contained review of the main results already proved, including the explicit geometrical construction of the equation of motion from the steepest-entropy-ascent ansatz and its exact mathematical and conceptual equivalence with the maximal-entropy-generation variational-principle formulation presented in Gheorghiu-Svirschevski S 2001 *Phys. Rev. A* **63** 022105. Moreover, we show how it can be extended to the case of a composite system to obtain the general form of the equation of motion, consistent with the demanding requirements of strong separability and of compatibility with general thermodynamics principles. The irreversible term in the equation of motion describes the spontaneous attraction of the state operator in the direction of steepest entropy ascent, thus implementing the maximum entropy production principle in quantum theory. The time rate at which the path of steepest entropy ascent is followed has so far been left unspecified. As a step towards the identification of such rate, here we propose a possible, well-behaved and intriguing, general closure of the dynamics, compatible with the nontrivial requirements of strong separability. Based on the time–energy Heisenberg uncertainty relation, we derive a lower bound to the internal-relaxation-time functionals that determine the rate of entropy generation. This bound entails an upper bound to the rate of entropy generation. By this extreme maximal-entropy-generation-rate ansatz, each indivisible subsystem follows the direction of steepest locally perceived entropy ascent at the highest rate compatible with the time–energy uncertainty principle.

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1. Introduction

Recent discussions [1, 2, 3] on possible fundamental tests of standard unitary quantum mechanics, related to the existence of “spontaneous decoherence” at the microscopic level, are relevant to understanding and predicting decoherence in important future applications involving nanometric devices, fast switching times, clock synchronization, superdense coding, quantum computation, teleportation, quantum cryptography, etc. where entanglement structure and dynamics play a key role [4]. It has been suggested [1] that long-baseline neutrino oscillation experiments may provide means of testing the existence of spontaneous decoherence and, therefore, the validity of linear and nonlinear extensions of standard unitary QM. In this paper, we restrict our attention to extensions of standard QM that assume a “broader quantum kinematics”, i.e., an augmented set of true quantum states described by state operators ρ without the restriction $\rho^2 = \rho$, as recently re-proposed in this context [3, 5] and in other contexts [6].

To our knowledge, the first instance where this broader quantum kinematics has been considered is in the pioneering work by Hatsopoulos and Gyftopoulos [7], where an extension of standard QM was proposed so as to provide a non-statistical non-information-theoretic microscopic unification of mechanics and thermodynamics, based on the (revolutionary [8]) ansatz that, for any system, even if strictly isolated and uncorrelated: (1) the “true” quantum state (in the sense analogous to that of the wave function of standard quantum mechanics) is represented by a state operator ρ — a unit-trace, nonnegative-definite, hermitian operator on the Hilbert space \mathcal{H} associated with the system according to standard QM — belonging to a “broader quantum kinematics” that includes pure states ($\rho^2 = \rho$) as well as non-idempotent states ($\rho^2 \neq \rho$); and (2) the “physical” entropy (as opposed to a statistical or information-theoretic entropy related to incoherent stochastic mixtures of true states) is represented by the state functional $-k_B \text{Tr}(\rho \ln \rho)$. References [7, 9] give proofs that only this functional can represent the physical entropy in such context.

The present author, in [10, 11, 12, 13, 14, 15, 16, 17, 18] (see also [5, 19, 20, 21]), addressed the problem of deriving a well-behaved extension of the Schrödinger–von Neumann unitary dynamics meeting the very demanding set of strict requirements that appear to be necessary if one is willing to accept the Hatsopoulos–Gyftopoulos broader kinematics ansatz.

The equation of motion that we proposed and postulated in [10, 11] for the state operator ρ is rederived in the present paper by means of a the explicit geometrical construction also detailed in [12] that clarifies the steepest-entropy-ascent, i.e., maximum entropy production, feature already recognized in [13, 14, 15, 16, 17, 18]. Here, several new interesting additional features related to separability and correlations are proved. As a result, we also show how the equivalent variational formulation in [3] can be extended to the composite system case.

The nonlinear extension of the Schrödinger–von Neumann equation of motion is derived, together with a full discussion of the necessary notation and definitions, in section 3 for a single indivisible system, and in sections 10 and 11 for a general system consisting of M distinguishable indivisible subsystems. However, to support some preliminary and motivating discussion, and to single it out from the many equations in the paper, we anticipate here the display of the proposed equation of motion.

For a single indivisible system, the rate of change of the state operator is given by the sum of the usual unitary Hamiltonian term and a nonlinear, entropy-generating term

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \hat{\mathbf{D}}_1(\rho, H, G_i), \quad (1a)$$

$$\hat{\mathbf{D}}_1(\rho, H, G_i) = -\frac{1}{2\tau(\rho)}[\sqrt{\rho}D + D^\dagger\sqrt{\rho}], \quad (1b)$$

$$D = [\sqrt{\rho}(B \ln \rho)]_{\perp \mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H, [\sqrt{\rho}G_i]\}}, \quad (1c)$$

where (details in section 3) $[\sqrt{\rho}(B \ln \rho)]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}}$ denotes the component of operator $\sqrt{\rho}(B \ln \rho)$ orthogonal to the linear manifold $\mathcal{L}\{\sqrt{\rho}R_i\} = \mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H, [\sqrt{\rho}G_i]\}$ spanned by all real linear combinations of the set of operators $\{\sqrt{\rho}I, \sqrt{\rho}H, [\sqrt{\rho}G_i]\}$ where I is the identity operator on the Hilbert space \mathcal{H} of the system, $B \ln \rho$ the operator obtained from ρ

by substituting in its spectral expansion each nonzero eigenvalue p_i with $\ln p_i$, H the usual Hamiltonian operator associated with the system in standard QM, the G_i 's are additional (not always necessary) hermitian operators commuting with H that we call the non-Hamiltonian generators of the motion and that depend on the structure of the system, such as the i -th-type particle-number operators N_i for a Bose-Einstein or Fermi-Dirac field (in which case \mathcal{H} is a Fock space), or the total momentum component operators P_i of a free particle (in which case Gheorghiu-Svirschevski [3] proved Galileian invariance).

The Hamiltonian term in the equation of motion, $-i[H, \rho]/\hbar$, drives the state operator towards a unitary isoentropic evolution. The entropy-generating but energy-conserving nonunitary term $\hat{\mathbf{D}}_1(\rho, H, G_i)$, instead, drives the state operator towards the local direction of steepest entropy ascent (which is orthogonal to the direction of unitary evolution) compatible with mean values of the non-Hamiltonian time-invariants. Indeed, for a strictly isolated system, both terms maintain independently invariant the values of the trace, $\text{Tr}(\rho I) = 1$, the energy, $\text{Tr}(\rho H) = e(\rho)$, and the mean values of each non-Hamiltonian generator, $\text{Tr}(\rho G_i) = g_i(\rho)$, if any. In other words, the irreversible term pulls the state operator in the direction of the projection of the gradient of the entropy functional $-k_B \text{Tr}(\rho \ln \rho)$ onto the hyperplane of constant $\text{Tr}(\rho I)$, $\text{Tr}(\rho H)$, and $\text{Tr}(\rho G_i)$'s. Because the system is isolated, the entropy ceases to increase only when a local entropy maximum is reached, i.e., either an equilibrium state or a limit cycle.

For a general composite of indivisible subsystems, instead, the equation of motion takes the following form. The rate of change of the state operator is given by the sum of the usual unitary Hamiltonian term and a sum of nonlinear terms accounting for "irreversible internal redistribution along the path of locally maximal entropy generation" within each indivisible subsystem,

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \hat{\mathbf{D}}_M(\rho, H, G_i), \quad (2a)$$

$$\hat{\mathbf{D}}_M(\rho, H, G_i) = -\sum_{J=1}^M \frac{1}{2\tau_J(\rho)} [\sqrt{\rho_J} D_J + D_J^\dagger \sqrt{\rho_J}] \otimes \rho_{\bar{J}}, \quad (2b)$$

$$D_J = [\sqrt{\rho_J} (B \ln \rho)^J]_{\perp \mathcal{L}\{\sqrt{\rho_J} I_J, \sqrt{\rho_J} (H)^J, [\sqrt{\rho_J} (G_i)^J]\}}. \quad (2c)$$

where $(F)^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}})F]$, for $F = B \ln \rho$, H , and G_i , and the other details are defined in sections 10 and 11 where we prove that all the necessary requirements (listed in Appendix A) for a self-consistent and well-defined extension of the Schrödinger–von Neumann equation of motion compatible with thermodynamic requirements are satisfied, together with a set of very intriguing mathematical properties and consistent physical consequences.

In [16], we realized that the internal-relaxation times $\tau_J(\rho)$ need not be constants (as initially assumed in [11]) but can be positive functionals of ρ . In sections 10 and 11, we note that these functionals must satisfy conditions of strong separability conceptually equivalent to those discussed by Czachor [2].

In section 7, we derive a lower bound for $\tau_J(\rho)$ which corresponds to the highest entropy generation rate compatible with the time–energy Heisenberg uncertainty principle. Taking the internal-relaxation times $\tau_J(\rho)$ exactly equal to these nontrivial lower bounds turns out to be compatible with the separability condition, and would complete the nonlinear dynamics in a general way with no need to assume the existence of new physical constants. Not only, then, the state would evolve along the path of steepest entropy ascent, but it would do so at the highest rate compatible with the time–energy uncertainty principle. However, other less extreme options are equally compatible.

We emphasize that the nonlinearity of the dynamics is such that one should not expect that the form of the equation valid for a single elementary (indivisible) constituent of matter be valid also for a system with an internal structure, because the equation of motion must reflect such structure not only through the Hamiltonian operator. However, of course, the superoperator $\hat{\mathbf{D}}_M$ reduces to $\hat{\mathbf{D}}_1$ [see (108) below] when the system has only one indivisible subsystem.

To make the paper self-contained, in section 6 we briefly review the fundamental unifying extensions to all nonequilibrium (dissipative) states of the Onsager reciprocity relations [22] and Callen's fluctuation-dissipation theorem [23] that derive from (1) [16] as well as, in general, from (2) [18].

In Appendix A and Appendix B, we discuss a set of criteria and the definition of stability of equilibrium that a fundamental dynamics must satisfy in order to be compatible with second law and other thermodynamic requirements. In the other appendixes, we discuss some extensions of the mathematics of (1) and (2).

2. The augmented state domain ansatz

The fundamental ansatz that the postulates of quantum mechanics can be successfully supplemented by the first and second principles of thermodynamics by assuming a broader state domain that includes not only $\rho^2 = \rho$ but also $\rho^2 \neq \rho$ state operators, provided that the functional $-k_B \text{Tr}(\rho \ln \rho)$ is taken for the physical entropy, was first proposed (without a dynamical law) by Hatsopoulos and Gyftopoulos [7].

Thirty years ago, the hypothesis of a state domain augmented with respect to that of traditional QM was perceived as adventurous [19] and countercurrent to the prevailing approaches to dissipative quantum dynamics within the frameworks of statistical, stochastic, phenomenological, information-theoretic, chaotic-behavior and bifurcation theories. For this reason, the broader quantum kinematics ansatz [7] and, five years later, the new nonlinear equation of motion have been considered initially as unphysical and substantially ignored (except for a few exceptions [19, 20, 21]), mainly because their motivation appeared to be derived from theoretical reasoning only (for example as recently summarized in [24]).

In search for direct experimental evidence, we derived explicit solutions for a two-level system and computed the effects of the irreversible atomic relaxation implied by the nonlinear equation of motion onto some basic quantum-electrodynamics results on absorption, stimulated emission, and resonance fluorescence from a single two-level atom [14, 15]. The results were obtained in the near-equilibrium linear limit and, of course, in terms of the yet undetermined internal-relaxation-time functional $\tau(\rho)$ that is part of the equation of motion. To our knowledge no one has yet attempted to verify these results experimentally and estimate $\tau(\rho)$.

The recent experimental evidence of loss of quantum coherence [2, 4, 25, 26] and the impressive effort devoted to study nonlinear modifications of the standard Schrödinger equation in the last forty years [27], finally seem to make more acceptable, if not require, the $\rho^2 \neq \rho$ augmented state domain Hatsopoulos–Gyftopoulos ansatz.

Once the $\rho^2 \neq \rho$ ansatz is accepted, the nonlinear equation of motion we proposed completes the dynamics and holds the promise to provide a microscopic-level explanation of the recent experimental evidence of loss of quantum coherence. It is with this motivation that Gheorghiu-Svirachevski [3] has “rediscovered” Eq. (1) together with many of its known features. [3] contributes to confirm the mathematical validity of this equation, including existence and uniqueness of solutions, and elegantly derives useful expansions and other results in the near-equilibrium linear limit. However, also in [3] the question of defining the form of the relaxation-time functional is left unresolved. A related development is also found in [28].

3. The steepest-entropy-ascent ansatz for an indivisible system

In [13, 16, 17], we emphasized that (1) and (2) have an important geometric interpretation. The Hamiltonian term, $-i[H, \rho]/\hbar$, and the irreversible term, $\hat{\mathbf{D}}_M(\rho, H, G_i)$ [or $\hat{\mathbf{D}}_1(\rho, H, G_i)$], compete with each other in the sense that the first drives the state operator towards a unitary motion tangent to the local constant entropy surface, whereas the second drives it towards the local direction of steepest entropy ascent along the surface with constant mean values of the generators of the motion. In this section, we show more explicitly than in the original papers how (1) can be constructed directly from the steepest-entropy-ascent ansatz.

Let \mathcal{H} ($\dim\mathcal{H} \leq \infty$) be the Hilbert space and H the Hamiltonian operator that are associated with the given (indivisible) elementary constituent system in standard QM. For simplicity, we first consider a system composed of a single elementary constituent. The nontrivial generalization to M constituents is given in section 10.

We assume that the (true) quantum states are one-to-one with the linear hermitian operators ρ on \mathcal{H} with $\text{Tr}(\rho) = 1$ and $\rho \geq 0$. As done in [11], we introduce the square-root state operator $\sqrt{\rho}$ obtained from the spectral expansion of ρ by substituting its eigenvalues with their positive square roots [30].

As a first step to force positivity and hermiticity of the state operator ρ we assume that the equation of motion may be written as

$$\frac{d\rho}{dt} = \sqrt{\rho} E + E^\dagger \sqrt{\rho} \quad (3)$$

where the operator E , in general non-hermitian, is defined below after introducing some necessary notation.

We consider the space $\mathcal{L}(\mathcal{H})$ of linear operators on \mathcal{H} equipped with the real scalar product

$$(F|G) = \frac{1}{2} \text{Tr}(F^\dagger G + G^\dagger F) . \quad (4)$$

so that for any (time-independent) hermitian R in $\mathcal{L}(\mathcal{H})$ the corresponding mean-value state functional, its local gradient operator with respect to $\sqrt{\rho}$, and its rate of change are

$$r(\rho) = \text{Tr}(\rho R) = (\sqrt{\rho}|\sqrt{\rho}R) , \quad (5)$$

$$\nabla_{\sqrt{\rho}} r(\rho) = \frac{\partial r(\rho)}{\partial \sqrt{\rho}} = \sqrt{\rho} R + R \sqrt{\rho} , \quad (6)$$

$$\frac{dr(\rho)}{dt} = \text{Tr}\left(\frac{d\rho}{dt} R\right) = 2 (E|\sqrt{\rho}R) . \quad (7)$$

Moreover, the entropy state functional, its gradient operator with respect to $\sqrt{\rho}$, and its rate of change are

$$s(\rho) = -k_B \text{Tr}(\rho \ln \rho) = -k_B (\sqrt{\rho}|\sqrt{\rho} \ln \rho) , \quad (8)$$

$$\nabla_{\sqrt{\rho}} s(\rho) = \frac{\partial s(\rho)}{\partial \sqrt{\rho}} = -2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho] , \quad (9)$$

$$\frac{ds(\rho)}{dt} = -k_B \left[\text{Tr}\left(\frac{d\rho}{dt}\right) + \text{Tr}\left(\frac{d\rho}{dt} \ln \rho\right) \right] = \left(E \left| \frac{\partial s(\rho)}{\partial \sqrt{\rho}} \right. \right) = \left(\frac{\partial s(\rho)}{\partial \sqrt{\rho}} \left| E \right. \right) . \quad (10)$$

Now it is easy to see from (7) that the values of the mean functionals $r_i(\rho)$ are time invariant if and only if E is orthogonal to $\sqrt{\rho} R_i$, for all i , i.e., if it is orthogonal to the linear manifold $\mathcal{L}\{\sqrt{\rho} R_i\}$ spanned by the set of operators $\{\sqrt{\rho} R_i\}$ in which we always have $\sqrt{\rho} R_0 = \sqrt{\rho} I$ (to preserve $\text{Tr}\rho = 1$) and $\sqrt{\rho} R_1 = \sqrt{\rho} H$ (to conserve energy), plus the additional non-Hamiltonian generators of the motion as already discussed.

It is noteworthy that

$$E_H = \frac{i}{\hbar} \sqrt{\rho} [H + c(\rho)I] , \quad (11)$$

with $c(\rho)$ any real functional of ρ , yields [through (3)] the Hamiltonian part of the equation of motion, and is orthogonal to $\mathcal{L}\{\sqrt{\rho} R_i\}$ as well as to the entropy gradient $\partial s(\rho)/\partial \sqrt{\rho}$.

Introducing the notation [16]

$$\Delta F = F - \text{Tr}(\rho F)I , \quad (12)$$

$$\langle \Delta F \Delta G \rangle = \langle \Delta G \Delta F \rangle = (\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta G) = \frac{1}{2} \text{Tr}(\rho \{\Delta F, \Delta G\}) , \quad (13)$$

for F and G hermitian in $\mathcal{L}(\mathcal{H})$ and $\{\cdot, \cdot\}$ the usual anticommutator, and defining the shortest characteristic time associated with the Hamiltonian part of the equation of motion by the relation (see Appendix C)

$$\frac{1}{\tau_H(\rho)^2} = 4 (E_H | E_H) , \quad (14)$$

we find, from (11) and $(\sqrt{\rho}|\sqrt{\rho}) = 1$,

$$\tau_H(\rho)^2 \langle \Delta H \Delta H \rangle = \hbar^2/4 - [c(\rho) + \text{Tr}(\rho H)]^2 \tau_H(\rho)^2, \quad (15)$$

so that only the choice $c = -e(\rho) = -\text{Tr}(\rho H)$ is compatible with the Heisenberg time-energy uncertainty relation $\tau_H(\rho)^2 \langle \Delta H \Delta H \rangle \geq \hbar^2/4$ which is then satisfied with strict equality. Therefore,

$$E_H = \frac{i}{\hbar} \sqrt{\rho} \Delta H, \quad (16)$$

and

$$\tau_H(\rho)^2 \langle \Delta H \Delta H \rangle = \hbar^2/4. \quad (17)$$

We may note that the foregoing discussion on the choice of $c(\rho)$ is somewhat artificial because any $c(\rho)$ cancels out in (3). However, the line of thought becomes important when we apply it later to the irreversible part of the dynamics.

For the general rate of change of the state operator, we let

$$E = E_H + E_D, \quad (18)$$

so that (3) may be rewritten as

$$\frac{D\rho}{Dt} = \frac{d\rho}{dt} + \frac{i}{\hbar} [H, \rho] = \sqrt{\rho} E_D + E_D^\dagger \sqrt{\rho}, \quad (19)$$

and we assume E_D orthogonal to $\mathcal{L}\{\sqrt{\rho}R_i\}$ but in the direction of the entropy gradient operator. We cannot take E_D directly proportional to $\partial s(\rho)/\partial\sqrt{\rho}$ as such, because the entropy gradient in general has a component along $\mathcal{L}\{\sqrt{\rho}R_i\}$ which would not preserve the mean values of the generators of the motion. We must take E_D proportional to the component of the entropy gradient orthogonal to $\mathcal{L}\{\sqrt{\rho}R_i\}$, namely, for the indivisible system,

$$E_D = \frac{1}{4k_B\tau(\rho)} \left[\frac{\partial s(\rho)}{\partial\sqrt{\rho}} \right]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}} \quad (20a)$$

$$= \frac{1}{4k_B\tau(\rho)} \left(\frac{\partial s(\rho)}{\partial\sqrt{\rho}} - \left[\frac{\partial s(\rho)}{\partial\sqrt{\rho}} \right]_{\mathcal{L}\{\sqrt{\rho}R_i\}} \right) \quad (20b)$$

$$= -\frac{1}{2\tau(\rho)} \left(\sqrt{\rho} \ln \rho - [\sqrt{\rho} \ln \rho]_{\mathcal{L}\{\sqrt{\rho}R_i\}} \right) \quad (20c)$$

$$= -\frac{1}{2\tau(\rho)} D \quad (20d)$$

where $[\partial s(\rho)/\partial\sqrt{\rho}]_{\mathcal{L}\{\sqrt{\rho}R_i\}}$ denotes the projection of $\partial s(\rho)/\partial\sqrt{\rho}$ onto $\mathcal{L}\{\sqrt{\rho}R_i\}$ and

$$D = \sqrt{\rho} \ln \rho - [\sqrt{\rho} \ln \rho]_{\mathcal{L}\{\sqrt{\rho}R_i\}} \quad (21a)$$

$$= [\sqrt{\rho} \ln \rho]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}} \quad (21b)$$

$$= \frac{\begin{vmatrix} \sqrt{\rho} \ln \rho & \sqrt{\rho} R_0 & \cdots & \sqrt{\rho} R_i & \cdots \\ (\sqrt{\rho} \ln \rho | \sqrt{\rho} R_0) & (\sqrt{\rho} R_0 | \sqrt{\rho} R_0) & \cdots & (\sqrt{\rho} R_i | \sqrt{\rho} R_0) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ (\sqrt{\rho} \ln \rho | \sqrt{\rho} R_i) & (\sqrt{\rho} R_0 | \sqrt{\rho} R_i) & \cdots & (\sqrt{\rho} R_i | \sqrt{\rho} R_i) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\Gamma(\{\sqrt{\rho}R_i\})} \quad (21c)$$

$$= -\frac{1}{k_B} \frac{\begin{vmatrix} \sqrt{\rho}\Delta S & \sqrt{\rho}\Delta R_1 & \cdots & \sqrt{\rho}\Delta R_i & \cdots \\ \langle \Delta S \Delta R_1 \rangle & \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_i \Delta R_1 \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta S \Delta R_i \rangle & \langle \Delta R_1 \Delta R_i \rangle & \cdots & \langle \Delta R_i \Delta R_i \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\Gamma(\{\sqrt{\rho}R_i\})} \quad (21d)$$

where in writing the last equation, which follows [29] from the well-known properties of determinants together with (12) and (13) and the fact that $R_0 = I$, we defined for convenience the entropy operator

$$S = -k_B B \ln \rho = -k_B \ln(\rho + I - B) \quad (22a)$$

with B obtained from ρ by substituting in its spectral expansion each nonzero eigenvalue with unity, i.e., more formally, $B = B^2 = P_{\text{Ran } \rho} = I - P_{\text{Ker } \rho} = P_{\perp \text{Ker } \rho}$, so that

$$B = B^2, \quad [B, \rho] = 0, \quad B\rho = \rho. \quad (22b)$$

Because operator B is the projector onto the range of ρ (and $I - B$ the projector onto the kernel of ρ) it is easy to show that S is well defined for any ρ , even if singular. In particular, when $\rho^2 = \rho$, S is the null operator.

The Gram determinant at the denominator,

$$\Gamma(\{\sqrt{\rho}R_i\}) = \det[\{(\sqrt{\rho}R_i|\sqrt{\rho}R_j)\}] \quad (23a)$$

$$= \begin{vmatrix} (\sqrt{\rho}R_0|\sqrt{\rho}R_0) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}R_0) & \cdots \\ \vdots & \ddots & \vdots & \ddots \\ (\sqrt{\rho}R_0|\sqrt{\rho}R_i) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}R_i) & \cdots \\ \vdots & \ddots & \vdots & \ddots \end{vmatrix} \quad (23b)$$

$$= \det[\{\langle \Delta R_{i>0} \Delta R_{j>0} \rangle\}] \quad (23c)$$

$$= \begin{vmatrix} \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_i \Delta R_1 \rangle & \cdots \\ \vdots & \ddots & \vdots & \ddots \\ \langle \Delta R_1 \Delta R_i \rangle & \cdots & \langle \Delta R_i \Delta R_i \rangle & \cdots \\ \vdots & \ddots & \vdots & \ddots \end{vmatrix}, \quad (23d)$$

is always strictly positive by virtue of the linear independence of the operators in the set $\{\sqrt{\rho}R_i\}$.

By the well-known properties of determininats, it is easy to verify that E_H and E_D are orthogonal, i.e., $(E_D|E_H) = 0$, and that the mean value of each R_i is conserved, i.e., $(E_D|\sqrt{\rho}R_i) = 0$, therefore, $\text{Tr}(\rho I)$, $\text{Tr}(\rho H)$, and the $\text{Tr}(\rho G_i)$'s are constants of the motion.

A further, compact expression can be written if we choose a set of operators $\{\sqrt{\rho}A_i\}$ which like the set $\{\sqrt{\rho}R_i\}$ spans $\mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H, [\sqrt{\rho}G_i]\}$ but, in addition, forms an orthonormal set, e.g., obtained from $\sqrt{\rho}I$, $\sqrt{\rho}H$, $\sqrt{\rho}G_i$ by a Gram-Schmidt orthogonalization procedure followed by normalization. For example,

$$A_1 = I, \quad (24a)$$

$$A_2 = \frac{\Delta H}{\sqrt{\langle \Delta H \Delta H \rangle}}, \quad (24b)$$

$$A_3 = \frac{\langle \Delta H \Delta H \rangle \Delta G_1 - \langle \Delta H \Delta G_1 \rangle \Delta H}{\sqrt{\langle \Delta H \Delta H \rangle [\langle \Delta H \Delta H \rangle \langle \Delta G_1 \Delta G_1 \rangle - \langle \Delta H \Delta G_1 \rangle^2]}}, \quad (24c)$$

...

Then,

$$(\sqrt{\rho}A_i|\sqrt{\rho}A_j) = \delta_{ij}, \quad (25a)$$

$$a_i(\rho) = (\sqrt{\rho}A_i|\sqrt{\rho}A_i) = \delta_{i1} , \quad (25b)$$

$$D = \sqrt{\rho} \ln \rho - \sum_{i=1}^a (\sqrt{\rho} \ln \rho | \sqrt{\rho} A_i) \sqrt{\rho} A_i , \quad (25c)$$

$$\Gamma(\{\sqrt{\rho}A_i\}) = 1 . \quad (25d)$$

It is noteworthy that operators A_i are nonlinear functions of ρ and, therefore, in general, vary with ρ as it evolves with time.

We finally obtain the following equivalent expressions for the rate of entropy change

$$\frac{ds(\rho)}{dt} = \frac{1}{4k_B\tau(\rho)} \left(\left[\frac{\partial s(\rho)}{\partial \sqrt{\rho}} \right]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} \left[\frac{\partial s(\rho)}{\partial \sqrt{\rho}} \right]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} \right) \quad (26a)$$

$$= 4k_B\tau(\rho) (E|E) \quad (26b)$$

$$= 4k_B\tau(\rho) (E_D|E_D) \quad (26c)$$

$$= \frac{1}{k_B\tau(\rho)} \left[\langle \Delta S \Delta S \rangle - \sum_{i=1}^a (\langle \Delta S \Delta A_i \rangle)^2 \right] \quad (26d)$$

$$= \frac{k_B}{\tau(\rho)} (D|D) \quad (26e)$$

$$= \frac{k_B}{\tau(\rho)} \frac{\Gamma(\sqrt{\rho} \ln \rho, \{\sqrt{\rho}R_i\})}{\Gamma(\{\sqrt{\rho}R_i\})} \quad (26f)$$

$$= \frac{1}{k_B\tau(\rho)} \frac{\Gamma(\sqrt{\rho}S, \{\sqrt{\rho}R_i\})}{\Gamma(\{\sqrt{\rho}R_i\})} \quad (26g)$$

where the Gram determinant

$$\Gamma(\sqrt{\rho}S, \{\sqrt{\rho}R_i\}) = \begin{vmatrix} (\sqrt{\rho}S|\sqrt{\rho}S) & (\sqrt{\rho}R_0|\sqrt{\rho}S) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}S) & \cdots \\ (\sqrt{\rho}S|\sqrt{\rho}R_0) & (\sqrt{\rho}R_0|\sqrt{\rho}R_0) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}R_0) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ (\sqrt{\rho}S|\sqrt{\rho}R_i) & (\sqrt{\rho}R_0|\sqrt{\rho}R_i) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}R_i) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix} \\ = \begin{vmatrix} \langle \Delta S \Delta S \rangle & \langle \Delta R_1 \Delta S \rangle & \cdots & \langle \Delta R_i \Delta S \rangle & \cdots \\ \langle \Delta S \Delta R_1 \rangle & \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_i \Delta R_1 \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta S \Delta R_i \rangle & \langle \Delta R_1 \Delta R_i \rangle & \cdots & \langle \Delta R_i \Delta R_i \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix} \quad (27)$$

is also strictly positive [except when ρ satisfies (28), see below].

Whereas the unitary Hamiltonian term in (1) maintains unchanged all the eigenvalues of ρ , the irreversible term maintains zero the initially zero eigenvalues of ρ and, therefore, conserves the cardinality of the set of zero eigenvalues, $\dim \text{Ker}(\rho)$ (for proofs see [3, 11]). In other words, the equation of motion preserves the rank and nullity of ρ . If the isolated system is prepared in a state that does not 'occupy' the eigenvector $|\psi_\ell\rangle$ of H (and the G_i 's), i.e., if $\rho(0)|\psi_\ell\rangle = 0$ (so that $|\psi_\ell\rangle$ is also an eigenvector of ρ corresponding to a zero eigenvalue), then such energy eigenvector remains 'unoccupied' at all times, i.e., $\rho(t)|\psi_\ell\rangle = 0$, the null space of ρ is an invariant of the motion.

This condition preserves an important feature that in standard QM allows remarkable model simplifications: the dynamics is fully equivalent to that of a model system with Hilbert space \mathcal{H}' (a subspace of \mathcal{H}) defined by the linear span of all the $|\psi_\ell\rangle$'s such that $\rho(t)|\psi_\ell\rangle \neq 0$ at some time t (and, hence, by our condition, at all times). The relevant operators X'

on \mathcal{H}' (ρ' , H' , G'_i , ...) are defined from the original X on \mathcal{H} (ρ , H , G_i , ...) so that $\langle \alpha_k | X' | \alpha_\ell \rangle = \langle \alpha_k | X | \alpha_\ell \rangle$ with $|\alpha_k\rangle$ any basis of \mathcal{H}' .

It is also consistent with recent experimental tests [31] that rule out, for pure states, deviations from linear and unitary dynamics and confirm that initially unoccupied eigenstates cannot spontaneously become occupied. This fundamental intrinsic feature of our extended microscopic dynamics adds nontrivial experimental and conceptual difficulty to the problem of designing a fundamental test of QM, but preserves within the extended theory the exact validity of all the remarkable successes of QM.

4. Nondissipative states and limit cycles: the Schrödinger–von Neumann limit

Eq. (1) reduces to the Schrödinger–von Neumann equation of motion, $i\hbar\dot{\rho} = [H, \rho]$, when $\rho^2 = \rho$ (thus entailing the usual unitary hamiltonian dynamics of standard QM), and also when and only when

$$\rho_{\text{nd}} = \frac{B \exp(C)}{\text{Tr}[B \exp(C)]}, \quad B^2 = B, \quad [B, C] = 0, \quad (28)$$

or, equivalently,

$$\sqrt{\rho_{\text{nd}}} \ln \rho_{\text{nd}} = \sqrt{\rho_{\text{nd}}} C - \sqrt{\rho_{\text{nd}}} \ln \text{Tr}[B \exp(C)], \quad (29)$$

where

$$C = -\beta H + \sum_i \nu_i G_i, \quad (30)$$

in which case we say that the state is nondissipative, and the solution of the equation of motion is

$$\rho_{\text{nd}}(t) = B(t) \exp(C) / \text{Tr}[B(t) \exp(C)], \quad (31a)$$

$$B(t) = U(t) B(0) U^{-1}(t), \quad U(t) = \exp(-itH/\hbar), \quad (31b)$$

which includes the usual $\rho^2 = \rho$ Schrödinger dynamics when C is the null operator [$\beta = \nu_i = 0$ in (28)] and, therefore, $\text{Tr}(B) = 1$.

Nondissipative states (28) have a thermal-like distribution (with positive or negative temperatures) over a finite number, $\text{Tr}(B)$, of “occupied” eigenvectors. Because entropy cannot decrease and $s(\rho)$ is an S -function [32], they are conditionally locally stable equilibrium states or limit cycles. They constitute the “target” highest-entropy states compatible with the mean values of the invariant functionals and the invariant null subspace of unoccupied eigenvectors.

For an initial state ρ commuting with H , i.e., for $[B(0), H] = 0$, by interpreting the entropy $s(\rho)$ as a measure of how “well” the energy is distributed within the isolated system among the available energy levels, the nonlinear dynamics describes a spontaneous internal redistribution of the energy along the path of maximal entropy increase leading towards an “optimally” distributed (highest entropy) state compatible with the condition of maintaining unoccupied the initially unoccupied energy levels.

When $[B(0), H] = 0$ the nondissipative state is an equilibrium state [or stationary state, if $H = H(t)$]. When $[B(0), H] \neq 0$, instead, the unitary evolution in (31) can be regarded as a (constant entropy) limit cycle (or “ridge” as termed in [3]), which coincides with the usual periodic solutions of the Schrödinger equation when B is a one-dimensional projector, $B = |\psi\rangle\langle\psi|$ [$\text{Tr}(B) = 1$].

The equation of motion attracts the state operator towards such highest entropy state or limit cycle by rearranging the nonzero eigenvalues of ρ along the direction of steepest entropy ascent at a rate that depends on the value of internal-relaxation-time functional $\tau(\rho)$. A minor perturbation of the state that changes an initially zero eigenvalue to an arbitrarily small nonzero value would cause an irreversible departure of the state towards a different equilibrium state or limit cycle. Hence, by the definition of stability according to Lyapunov, as long as there are zero eigenvalues of ρ , i.e., unless $B = I$, all equilibrium states and limit

cycles are unstable. Without this conclusion, we could not claim that the equation of motion entails the second law of thermodynamics (see Appendix A and Appendix B, and [7, 11, 13, 32], for further discussions of this important point). The question of whether the equation could admit of metastable equilibrium states has not yet been investigated.

The Hamiltonian operator may be set to vary with time in order to model (adiabatic) energy exchange with the surroundings. Then the unitary part of the equation of motion, $-i[H(t), \rho]/\hbar$, may model energy change, but not entanglement nor entropy exchange with the surroundings. The irreversible term, instead, describes internal relaxation only and does not contribute to energy change in any case.

5. Highest-entropy equilibrium states

The only globally stable equilibrium states of the dynamics generated by (1) are

$$\rho_e = \frac{\exp(C)}{\text{Tr} \exp(C)} = \frac{\exp(-\beta H + \sum_i \nu_i G_i)}{\text{Tr} \exp(-\beta H + \sum_i \nu_i G_i)}. \quad (32)$$

The definition of global stability, which is stronger than Lyapunov or local stability and is required by the second law [32, 33], is given and discussed in Appendix B. The proof was discussed in [11, 14, 32].

For a system with generators of the motion I, H, N_i , (32) represents in general the grand canonical thermodynamic equilibrium states. It reduces to the canonical equilibrium states if $N_i = \tilde{n}_i I$ for all i 's (to the microcanonical if also $H = \tilde{e}I$).

As is well known, states given by (32) are solutions of the constrained maximization problem

$$\max s(\rho) \quad \text{subject to} \quad r_i(\rho) = \tilde{r}_i \text{ and } \rho \geq 0, \quad (33)$$

where $s(\rho) = -k_B \text{Tr}(\rho \ln \rho)$, $r_1(\rho) = \text{Tr}(\rho I)$, $r_2(\rho) = \text{Tr}(\rho H)$, $r_i(\rho) = \text{Tr}(\rho G_i)$, $\tilde{r}_1 = 1$, \tilde{r}_2 and \tilde{r}_i 's given.

The inequality constraint $\rho \geq 0$ can be eliminated recasting the problem in terms of $\sqrt{\rho}$,

$$\max s(\sqrt{\rho}) \quad \text{subject to} \quad r_i(\sqrt{\rho}) = \tilde{r}_i, \quad (34)$$

where $s(\sqrt{\rho}) = -k_B \text{Tr}[(\sqrt{\rho})^2 \ln(\sqrt{\rho})^2] = s(\rho)$ and $r_i(\sqrt{\rho}) = \text{Tr}[(\sqrt{\rho})^2 R_i] = r_i(\rho)$. The method of Lagrange multipliers then gives the condition (necessary but not sufficient)

$$\frac{\partial s(\rho)}{\partial \sqrt{\rho}} - \sum_i \lambda_i \frac{\partial r_i(\rho)}{\partial \sqrt{\rho}} = 0, \quad (35)$$

which, using (6) and (9), becomes

$$-2k_B \sqrt{\rho} \ln \rho - 2k_B \sqrt{\rho} - \sum_i \lambda_i (\sqrt{\rho} R_i + R_i \sqrt{\rho}) = 0. \quad (36)$$

It is noteworthy that (36) is satisfied with obvious identification of multipliers by (29), where $\sum_i \lambda_i \sqrt{\rho} R_i$ commutes with $\sqrt{\rho} \ln \rho$, i.e., with ρ . Therefore, each nondissipative state satisfies the necessary condition (36) although it is not a solution of the maximization problem (34) unless $B = I$.

6. Onsager's reciprocity and Callen's fluctuation-dissipation nonequilibrium relations

First, we introduce a general representation of state operators particularly useful for representing nonequilibrium states. Any ρ can be written as [16]

$$\rho = \frac{B \exp(-\sum_j f_j X_j / k_B)}{\text{Tr} B \exp(-\sum_j f_j X_j / k_B)}, \quad (37)$$

where the hermitian operators in the set $\{I, X_j\}$ span the real space $\mathcal{L}_h(\mathcal{H})$ of linear hermitian operators on \mathcal{H} , and B is the usual idempotent operator defined in (22b). Indeed, the operator $B \ln \rho$ is always well-defined and belongs to $\mathcal{L}_h(\mathcal{H})$, so that

$$S = -k_B B \ln \rho = f_0 I + \sum_j f_j X_j = f_0 B I + \sum_j f_j B X_j \quad (38)$$

where the second equality follows from $B^2 = B$ and f_0 is a generalized log-partition function

$$f_0 = k_B \ln \text{Tr} B \exp\left(-\sum_j f_j X_j / k_B\right). \quad (39)$$

Therefore,

$$-k_B \sqrt{\rho} \ln \rho = f_0 \sqrt{\rho} + \sum_j f_j \sqrt{\rho} X_j, \quad (40)$$

$$x_j(\rho) = \text{Tr}(\rho X_j), \quad (41)$$

$$\sqrt{\rho} \Delta S = \sum_i f_i \sqrt{\rho} \Delta X_i, \quad (42)$$

$$\langle \Delta S \Delta S \rangle = \sum_i \sum_j f_i f_j \langle \Delta X_i \Delta X_j \rangle, \quad (43)$$

$$s(\rho) = f_0 + \sum_j f_j x_j(\rho), \quad (44)$$

$$k_B D = -\sum_j f_j \left[\sqrt{\rho} X_j - \sum_{k=1}^a (\sqrt{\rho} X_j | \sqrt{\rho} A_k) \sqrt{\rho} A_k \right] \quad (45)$$

where, for simplicity, we use the expression (25c) for D in terms of the orthonormal set $\{\sqrt{\rho} A_i\}$ [an equivalent expression in terms of Gram determinants is readily obtained using (40) in (21c)].

By taking partial derivatives of a symmetrized expansion of f_0 , we may also obtain the relations $x_j(\rho) = \partial f_0 / \partial f_j$ and, equating second order partial derivatives, the generalized Maxwell relations

$$\left. \frac{\partial x_i(\rho)}{\partial f_j} \right|_{f_{k \neq j}} = -\frac{1}{k_B} \langle \Delta X_i \Delta X_j \rangle = \left. \frac{\partial x_j(\rho)}{\partial f_i} \right|_{f_{k \neq i}}. \quad (46)$$

It is noteworthy that state operator (37) can be viewed as the solution of the constrained maximization problem

$$\max s(\rho) \quad (47a)$$

$$\text{subject to } x_j(\rho) = \text{Tr}(\rho X_j) = \tilde{x}_j, \quad (47b)$$

$$\text{Tr}(\rho) = 1, \quad \rho \geq 0, \quad \text{and } \rho = B \rho B \quad (47c)$$

or, equivalently,

$$\max s(\sqrt{\rho}) \quad (48a)$$

$$\text{subject to } x_j(\sqrt{\rho}) = (\sqrt{\rho} | \sqrt{\rho} X_j) = \tilde{x}_j, \quad (48b)$$

$$(\sqrt{\rho} | \sqrt{\rho}) = 1, \quad \text{and } \sqrt{\rho} = B \sqrt{\rho} B \quad (48c)$$

for a given idempotent operator $B = B^2$ and given mean values \tilde{x}_j of the operators in the set $\{X_j\}$. As a result, the Lagrange multipliers f_j can be viewed as functions of the \tilde{x}_j 's, defined implicitly by the relations obtained by substitution of (37) into the constraints. Thus, the expression for the entropy can be written as

$$s(\tilde{\mathbf{x}}) = f_0(\tilde{\mathbf{x}}) + \sum_j f_j(\tilde{\mathbf{x}}) \tilde{x}_j \quad (49)$$

from which we readily obtain that

$$f_j = \left. \frac{\partial s(\tilde{\mathbf{x}})}{\partial \tilde{x}_j} \right|_{\tilde{x}_{k \neq j}} \quad (50)$$

may be interpreted as the generalized affinity or force representing the entropy change that corresponds to an independent change in the mean value of the linear observable X_j . Moreover, by equating second order partial derivatives of $s(\tilde{\mathbf{x}})$, we obtain the generalized Maxwell relations

$$\left. \frac{\partial f_i(\tilde{\mathbf{x}})}{\partial \tilde{x}_j} \right|_{\tilde{x}_k \neq j} = \frac{\partial^2 s(\tilde{\mathbf{x}})}{\partial \tilde{x}_i \partial \tilde{x}_j} = \left. \frac{\partial f_j(\tilde{\mathbf{x}})}{\partial \tilde{x}_i} \right|_{\tilde{x}_k \neq i} . \quad (51)$$

Next, we define the dissipative rate of change of the linear mean-value functional associated with operator X_i ,

$$\frac{Dx_i(\rho)}{Dt} = \text{Tr}[\hat{\mathbf{D}}_1(\rho, H, G_i)X_i] = 2(E_D | \sqrt{\rho}X_i) . \quad (52)$$

We use the term dissipative because the irreversible term in the equation of motion conserves but downgrades the energy, i.e., it describes the irreversible conversion (dissipation) of mechanical energy into thermal energy. Using $E_D = -D/2\tau(\rho)$ [(20d)] and (45) yields the linear interrelations between dissipative rates and generalized affinities,

$$\frac{Dx_i(\rho)}{Dt} = \sum_j f_j L_{ij}(\rho) , \quad (53)$$

where the coefficients $L_{ij}(\rho)$, which may be interpreted as generalized (Onsager) dissipative conductivities, are the nonlinear functionals of ρ given by the relations

$$L_{ij}(\rho) = L_{ji}(\rho) = \frac{1}{k_B \tau(\rho)} \left[(\sqrt{\rho}X_i | \sqrt{\rho}X_j) - \sum_{k=1}^a (\sqrt{\rho}X_i | \sqrt{\rho}A_k)(\sqrt{\rho}A_k | \sqrt{\rho}X_j) \right] \quad (54a)$$

$$= \frac{1}{k_B \tau(\rho)} \left[\langle \Delta X_i \Delta X_j \rangle - \sum_{k=1}^a \langle \Delta X_i \Delta A_k \rangle \langle \Delta A_k \Delta X_j \rangle \right] \quad (54b)$$

$$= \frac{1}{k_B \tau(\rho)} \left([\sqrt{\rho}X_i]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} | [\sqrt{\rho}X_j]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} \right) \quad (54c)$$

$$= \frac{1}{k_B \tau(\rho) \Gamma(\{\sqrt{\rho}R_k\})} \begin{vmatrix} \langle \Delta X_i \Delta X_j \rangle & \langle \Delta R_1 \Delta X_j \rangle & \cdots & \langle \Delta R_k \Delta X_j \rangle & \cdots \\ \langle \Delta X_i \Delta R_1 \rangle & \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_k \Delta R_1 \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta X_i \Delta R_k \rangle & \langle \Delta R_1 \Delta R_k \rangle & \cdots & \langle \Delta R_k \Delta R_k \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix} . \quad (54d)$$

These relations are at the same time a proof and a generalization of Onsager's reciprocity relations [22] extended to all nonequilibrium (dissipative) states. Moreover, they give explicit expressions for the nonlinear dependence of the dissipative conductivities $L_{ij}(\rho)$ on the state operator ρ , the generators of the motion and the internal-relaxation-time $\tau(\rho)$. Of course, at any stable equilibrium, ρ_e , and at any nondissipative state or limit cycle, ρ_{nd} , all dissipative rates are zero and, therefore,

$$\sum_j f_j \rho_{e/nd} L_{ij}(\rho_{e/nd}) = 0 . \quad (55)$$

Using (26) and (40), the rate of entropy change may be rewritten as a quadratic form in the generalized affinities,

$$\frac{ds(\rho)}{dt} = \sum_i f_i \frac{Dx_i(\rho)}{Dt} = \sum_i \sum_j f_i f_j L_{ij}(\rho) . \quad (56)$$

The symmetric matrix $\{L_{ij}(\rho)\}$ is a Gram matrix [see (54c)] and, as such, it is nonnegative definite, i.e., its determinant

$$\det\{L_{ij}(\rho)\} \geq 0, \quad (57)$$

with strict positivity only if all operators

$$[\sqrt{\rho}X_i]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} \quad (58)$$

are linearly independent, in which case (53) may be solved to yield

$$f_j = \sum_i L_{ij}^{-1}(\rho) \frac{Dx_i(\rho)}{Dt} \quad (59)$$

and the rate of entropy change can be written as a quadratic form in the dissipative rates

$$\frac{ds(\rho)}{dt} = \sum_i \sum_j L_{ij}^{-1}(\rho) \frac{Dx_i(\rho)}{Dt} \frac{Dx_j(\rho)}{Dt}. \quad (60)$$

Eqs. (54) are also a proof and generalization of Callen's fluctuation-dissipation theorem [23] extended to all nonequilibrium (dissipative) states. Indeed, we interpret $\langle \Delta X_i \Delta X_j \rangle$ as the codispersion (covariance) of measurement results of observables X_i and X_j when the system is in state ρ and $\langle \Delta X_i \Delta X_i \rangle$ as the dispersion (or fluctuations) of measurement results of observable X_i . As in Callen's fluctuation-dissipation theorem, the expressions in (54) relate codispersions with generalized conductivities.

A judicious choice of the set $\{\sqrt{\rho}X_j\}$ may greatly simplify these relations. In particular, if $\{\sqrt{\rho}X_j\}$ is any orthogonal extension of the orthonormal subset $\{\sqrt{\rho}A_i\}$, in the sense that $(\sqrt{\rho}X_j | \sqrt{\rho}A_i) = 0$ for all A_i 's and $j > a$, then for all i and $j > a$,

$$L_{ij}(\rho) = \frac{1}{k_B \tau(\rho)} \langle \Delta X_i \Delta X_j \rangle, \quad (61)$$

which relates directly [through the internal-relaxation time $\tau(\rho)$] covariances and fluctuations in the observables X_i with their associated dissipative conductivities.

Onsager's [22] and Callen's [23] theorems are keystones of our understanding of irreversibility. Indeed, the proof we proposed emerges not from the analysis of the Hamiltonian term of the equation of motion supplemented with the so-called assumption of microscopic reversibility, but from the irreversible term of the equation of motion, i.e., the only term responsible for irreversibility, with no additional assumptions.

Onsager's result [22] was obtained from empirical observations on nonequilibrium phenomena very close to stable thermodynamic equilibrium, so that the list of X_i 's was indeed very short, and the result valid only for a limited class of states. Our result generalizes the validity of Onsager's reciprocity relations to all nonequilibrium states, close and far from stable thermodynamic equilibrium. Of course, the price we have to pay to describe nonequilibrium states far from stable equilibrium is that we must use a much larger, possibly infinite list of X_i 's in (37).

7. Internal relaxation time vs time-energy Heisenberg uncertainty: maximal-entropy-generation-rate ansatz

By analogy with what was done for the Hamiltonian characteristic time $\tau_H(\rho)$, we define the shortest characteristic time of the irreversible part of the rate of change of the state operator by the relation (see Appendix C)

$$\frac{1}{\tau_D(\rho)^2} = 4(E_D | E_D). \quad (62)$$

From (20a) and (21) and $(\sqrt{\rho} | \sqrt{\rho}) = 1$ [or, directly, from (26)], we find

$$\tau_D(\rho)^2 = k_B^2 \tau(\rho)^2 \frac{\Gamma(\{\sqrt{\rho}R_i\})}{\Gamma(\sqrt{\rho}S, \{\sqrt{\rho}R_i\})} = \frac{\tau(\rho)^2}{(D|D)}. \quad (63)$$

From this relation we may extract a possible ansatz on the functional form or at least a lower bound for the internal-relaxation-time functional $\tau(\rho)$ in (1) by assuming that also $\tau_D(\rho)$, like $\tau_H(\rho)$, should satisfy the Heisenberg uncertainty relation

$$\tau_D(\rho)^2 \langle \Delta H \Delta H \rangle \geq \hbar^2/4 . \quad (64)$$

This implies

$$\tau(\rho)^2 \geq \frac{\hbar^2}{4k_B^2} \frac{\Gamma(\sqrt{\rho}S, \{\sqrt{\rho}R_i\})}{\langle \Delta H \Delta H \rangle \Gamma(\{\sqrt{\rho}R_i\})} = \frac{\hbar^2(D|D)}{4\langle \Delta H \Delta H \rangle} \quad (65)$$

or, using (26) and (56),

$$\tau(\rho) \geq \frac{\hbar^2}{4k_B \langle \Delta H \Delta H \rangle} \sum_i \sum_j f_i f_j L_{ij}(\rho) . \quad (66)$$

Relation (65) implies an upper bound to the rate of entropy generation,

$$\frac{ds(\rho)}{dt} \leq \frac{2}{\hbar} \sqrt{\frac{\langle \Delta H \Delta H \rangle \Gamma(\sqrt{\rho}S, \{\sqrt{\rho}R_i\})}{\Gamma(\{\sqrt{\rho}R_i\})}} . \quad (67)$$

By analogy with the Hamiltonian time, a possible ansatz that is worthy of careful consideration is that also $\tau_D(\rho)$ and, therefore, $\tau(\rho)$ be equal exactly to the lower bound [i.e., strict equality in (65), (66) and (67)], corresponding to the maximal entropy generation rate compatible with the time–energy uncertainty relation. This corresponds to a truly maximal entropy generation dynamics. The square-root state operator $\sqrt{\rho}$ not only moves in the direction of steepest entropy ascent, but it does so at the highest rate compatible with the uncertainty principle.

This ansatz is very intriguing, conceptually appealing and fraught with far-reaching physical consequences. But, like any other hypotheses on the functional form of $\tau(\rho)$, it should be verified against known behavior in worked-out specific cases, such as the examples considered in [3, 15, 20] and the variety of physical problems for which nonlinear modifications of the Schrödinger equation have been deemed necessary but have not yet been resolved [27].

If proved valid, this ansatz would complete the dynamics without need of additional physical constants and would provide a fundamental microscopic foundation of the macroscopic observation that Nature always evolves at the fastest possible rate along the most direct path towards maximum entropy compatible with the system's structure and external constraints. Interpreted in this way, our nonlinear dynamics would provide a unifying fundamental microscopic foundation of all phenomenological theories of irreversible processes advanced in the last seventy years after the pioneering work of Onsager.

8. Variational principle formulation

Following Gheorghiu-Svirachevski [3], the direction of steepest-entropy-ascent can also be found by considering the constrained maximization problem

$$\max \frac{ds}{dt}(E_D) \quad (68a)$$

$$\text{subject to } \frac{dr_i}{dt}(E_D) = \dot{r}_i \text{ and } (E_D|E_D) = \frac{1}{4\tau_D^2} , \quad (68b)$$

where \dot{r}_i and τ_D^2 are given real functionals of ρ . The necessary solving condition in terms of Lagrange multipliers is

$$\frac{\partial}{\partial E_D} \frac{ds}{dt} - \sum_i \lambda_i \frac{\partial}{\partial E_D} \frac{dr_i}{dt} - \lambda_0 \frac{\partial}{\partial E_D} (E_D|E_D) = 0 . \quad (69)$$

Using (7) and (10), it becomes

$$\frac{\partial s(\rho)}{\partial \sqrt{\rho}} - 2 \sum_i \lambda_i \sqrt{\rho} R_i - \lambda_0 E_D = 0 , \quad (70)$$

or, with (9),

$$-2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho] - 2 \sum_i \lambda_i \sqrt{\rho} R_i - \lambda_0 E_D = 0, \quad (71)$$

where the multipliers must be determined by substitution in the system of constraint equations.

It is easy to verify that our expression for $E_D = -D/2\tau(\rho)$ in (20a) and (21) is an explicit solution of (70) in the case $\dot{r}_i = 0$ and τ_D given by the explicit expression in (63). See Appendix E for $\dot{r}_i \neq 0$.

9. Bloch near-equilibrium linear limit

In [11] we have shown that in the neighbourhood of each equilibrium state ρ_e {given by (28) with the additional condition $[B, H] = 0$ }, if we assume $\tau(\rho)$ constant (e.g., $\tau_e = \tau(\rho_e) \neq 0$), the initial state operators $\rho(0)$ in the subset with $B(0) = B_e$ and $\text{Tr}(\rho(0)R_i) = \text{Tr}(\rho_e R_i)$ (i.e., with the same nullity, rank and mean values of the generators as the equilibrium state) obey a linearized form of the equation of motion that has the form of a Bloch relaxation equation,

$$\frac{d\rho}{dt} \rightarrow -\frac{i}{\hbar} [H, \rho] - \frac{\rho - \rho_e}{\tau_e}, \quad (72)$$

so that the solution of the equation of motion is

$$\rho(t) \rightarrow \exp(-t/\tau_e) U(t) \rho(0) U^{-1}(t) + [1 - \exp(-t/\tau_e)] \rho_e, \quad (73)$$

with $U(t)$ given by (31b) {note that if there are no non-Hamiltonian generators the condition $[B, C] = 0$ implies $[\rho, H] = 0$ and, therefore, $U(t)\rho(0)U^{-1}(t) = \rho(0)$ }.

Gheorghiu-Svirschevski [3], derived a more general linearized form for the case with no non-Hamiltonian generators valid also when $[\rho, H] \neq 0$ (but assuming $\tau \rightarrow \tau_e \neq 0$), and showed that it yields a generalized Fokker-Planck equation for a free particle, and a Langevin equation for a harmonic oscillator.

It is however noteworthy that such linearized limit behavior should be revised if we take $\tau(\rho)$ equal to the lower bound imposed by the time-energy uncertainty relation [(65) with strict equality], because then, if $\langle \Delta H \Delta H \rangle \neq 0$, $\tau(\rho) \rightarrow 0$ as $\rho \rightarrow \rho_e$.

10. Divisible composite systems dynamics: locally perceived overall energy and entropy operators

The composition of the system is embedded in the structure of the Hilbert space as a direct product of the subspaces associated with the individual elementary constituent subsystems, as well as in the form of the Hamiltonian operator.

In this section, we consider a system composed of M distinguishable and indivisible elementary constituent subsystems. For example, each subsystem may be a different elementary particle or a Fermi-Dirac or Bose-Einstein field (in which case the corresponding \mathcal{H}^J is a Fock space). The Hilbert space is

$$\mathcal{H} = \mathcal{H}^1 \otimes \mathcal{H}^2 \otimes \dots \otimes \mathcal{H}^M, \quad (74)$$

and the Hamiltonian operator

$$H = \sum_{J=1}^M H_J \otimes I_{\bar{J}} + V, \quad (75)$$

where H_J is the Hamiltonian operator on \mathcal{H}^J associated with the J -th subsystem when isolated and V (on \mathcal{H}) the interaction Hamiltonian among the M subsystems.

For convenience, we denote by $\mathcal{H}^{\bar{J}}$ the direct product of the Hilbert spaces of all subsystems except the J -th one, so that the Hilbert space of the overall system is

$$\mathcal{H} = \mathcal{H}^J \otimes \mathcal{H}^{\bar{J}} \quad (76)$$

and the identity operator $I = I_J \otimes I_{\bar{J}}$.

The subdivision into elementary constituents, each considered as indivisible, is reflected by the structure of the Hilbert space \mathcal{H} as a direct product of subspaces, and is particularly important because it defines the level of description of the system and specifies its elementary structure. This determines also the structure of the nonlinear dynamical law (2) we proposed in [10, 11] and rederive in the next section. In a sense, this is a price we have to pay in order to free ourselves from the assumption of linearity of the law of motion.

In other words, the form of superoperators $\hat{\mathbf{D}}_M$ and $\hat{\mathbf{D}}_1$ are different depending on whether the system is or is not subdivisible into indivisible subsystems, i.e., whether or not it has an internal structure. For example, consistently with the conditions listed in Appendix A, we request that superoperator $\hat{\mathbf{D}}_M$ satisfies the strong separability conditions [2, 20]

$$\begin{aligned} & \hat{\mathbf{D}}_M(\rho_A \otimes \rho_B, H_A \otimes I_B + I_A \otimes H_B, G_{iA} \otimes I_B + I_A \otimes G_{iB}) \\ &= \hat{\mathbf{D}}_{M_A}(\rho_A, H_A, G_{iA}) \otimes \rho_B + \rho_A \otimes \hat{\mathbf{D}}_{M_B}(\rho_B, H_B, G_{iB}) \text{ for any } \rho_A, \rho_B, \end{aligned} \quad (77a)$$

$$\begin{aligned} & \text{Tr}_B[\hat{\mathbf{D}}_M(\rho, H_A \otimes I_B + I_A \otimes H_B, G_{iA} \otimes I_B + I_A \otimes G_{iB})] \\ &= \hat{\mathbf{F}}_{M_A}(\rho, H_A, G_{iA}) \quad \text{for any } \rho, \end{aligned} \quad (77b)$$

$$\begin{aligned} & \text{Tr}_A[\hat{\mathbf{D}}_M(\rho, H_A \otimes I_B + I_A \otimes H_B, G_{iA} \otimes I_B + I_A \otimes G_{iB})] \\ &= \hat{\mathbf{F}}_{M_B}(\rho, H_B, G_{iB}) \quad \text{for any } \rho, \end{aligned} \quad (77c)$$

where subsystems A and B are obtained by partitioning the set of constituents $1, 2, \dots, M$ into two disjoint subsets of M_A and M_B constituents, respectively ($M_A + M_B = M$). Note that, of course, if $\rho = \rho_A \otimes \rho_B$ then we must have $\hat{\mathbf{F}}_{M_A}(\rho, H_A, G_{iA}) = \hat{\mathbf{D}}_{M_A}(\rho_A, H_A, G_{iA})$ and $\hat{\mathbf{F}}_{M_B}(\rho, H_B, G_{iB}) = \hat{\mathbf{D}}_{M_B}(\rho_B, H_B, G_{iB})$.

It is noteworthy that trying to apply the same conditions to superoperator $\hat{\mathbf{D}}_1$ would be physically meaningless. For a subdivisible system, $\hat{\mathbf{D}}_1$ cannot be the irreversible evolution superoperator because it would entail for example exchange of energy between noninteracting subsystems. Conditions (77b) and (77c) instead, prevent non-locality problems by guaranteeing that changes of the Hamiltonian (or the other generators of the motion) in one of two noninteracting subsystems cannot affect the mean values of local observables of the other subsystem. For example, assume that subsystems A and B are correlated but not interacting. We may switch on a measurement apparatus within B and therefore alter the Hamiltonian H_B . By virtue of (77b) and (77c), the rate of change of the reduced state operator $\rho_A = \text{Tr}_B(\rho)$ does not depend on H_B and, therefore, all the functionals of ρ_A (local observables) remain unaffected by the change in B , i.e., no faster-than-light communication can occur between B and A (of course, if we exclude the projection postulate [34]).

In addition, we must consider the following additional non-trivial conditions of separate energy conservation of noninteracting (possibly correlated) subsystems (see Appendix A, Condition 6)

$$\text{Tr}[(H_A \otimes I_B) \hat{\mathbf{D}}_M(\rho, H_A \otimes I_B + I_A \otimes H_B, G_i)] = 0, \quad (78a)$$

$$\text{Tr}[(I_A \otimes H_B) \hat{\mathbf{D}}_M(\rho, H_A \otimes I_B + I_A \otimes H_B, G_i)] = 0, \quad (78b)$$

for any ρ , and of separate entropy nondecrease for uncorrelated (possibly interacting) subsystems (see Appendix A, Condition 7)

$$\text{Tr}[(S_A \otimes I_B) \hat{\mathbf{D}}_M(\rho_A \otimes \rho_B, H, G_i)] \geq 0, \quad (79a)$$

$$\text{Tr}[(I_A \otimes S_B) \hat{\mathbf{D}}_M(\rho_A \otimes \rho_B, H, G_i)] \geq 0, \quad (79b)$$

for any ρ_A and ρ_B , where $S_A = -k_B B_A \ln \rho_A$, $S_B = -k_B B_B \ln \rho_B$.

For each type of particle in the system, we may write without loss of generality the number-of-particles-of- i -th-type operator associated with the system as

$$N_i = \sum_{J=1}^M N_{i,J} \otimes I_{\bar{J}} \quad \text{for } i = 1, 2, \dots, r, \quad (80)$$

where $N_{i,J}$ denotes the number-of-particles-of- i -th-type operator associated with the J -th subsystem [35]. In general, we assume that the set of linear hermitian operators I, H, G_i

on \mathcal{H} , always including I and H , are the generators of the motion of the composite system. For example, the list of non-Hamiltonian generators G_i may coincide with that of the number operators defined in (80).

Next, we introduce a useful notation that allows the definition of important local observables. For each subsystem J we denote by $\mathcal{L}(\mathcal{H}^J)$ the space of linear operators on \mathcal{H}^J equipped with the real scalar product

$$\langle F_J | G_J \rangle = \frac{1}{2} \text{Tr} \left(F_J^\dagger G_J + G_J^\dagger F_J \right) . \quad (81)$$

For a given state operator ρ on \mathcal{H} , given linear hermitian F and G on \mathcal{H} , and each subsystem J , in addition to that already defined in (4), (12) and (13), we define the following convenient notation [11, 16]

$$\rho_J = \text{Tr}_{\bar{J}}(\rho) , \quad (82)$$

$$\rho_{\bar{J}} = \text{Tr}_J(\rho) , \quad (83)$$

$$\langle F \rangle^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}}) F] , \quad (84)$$

$$\begin{aligned} \langle \Delta F \Delta G \rangle^J &= (\sqrt{\rho_J}(\Delta F)^J | \sqrt{\rho_J}(\Delta G)^J) \\ &= \frac{1}{2} \text{Tr}(\rho_J \{(\Delta F)^J, (\Delta G)^J\}) = \langle (\Delta F)^J (\Delta G)^J \rangle , \end{aligned} \quad (85)$$

where $\text{Tr}_{\bar{J}}$ denotes the partial trace over $\mathcal{H}^{\bar{J}}$, Tr_J over \mathcal{H}^J , ρ_J is the reduced state operator of elementary subsystem J and $\rho_{\bar{J}}$ that of the composite of all other subsystems.

In view of the special role they play in the equation of motion, we interpret the operators $(H)^J$ and $(S)^J$,

$$(H)^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}}) H] , \quad (86)$$

$$(S)^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}}) S] , \quad (87)$$

as “locally perceived overall-system energy” and “locally perceived overall-system entropy” operators, respectively, associated with a measure of how the overall-system energy and entropy operators, H and $S = -k_B B \ln \rho$, are “felt” locally within the J -th constituent subsystem.

For a given ρ_J , we further define the operators

$$\sqrt{\rho_J} , \quad (88)$$

$$B_J , \quad (89)$$

$$S_J = -k_B B_J \ln \rho_J , \quad (90)$$

obtained from ρ_J by substituting in its spectral expansion each nonzero eigenvalue p_i with its positive square root $\sqrt{p_i}$, unity and $-k_B \ln p_i$, respectively. Note that, of course, $S_J \neq (S)^J$. Moreover, for given linear hermitian F_J and G_J on \mathcal{H}^J , we define the notation

$$\langle F_J \rangle = \text{Tr}[\rho (F_J \otimes I_{\bar{J}})] = \text{Tr}(\rho_J F_J) , \quad (91)$$

$$\langle \Delta F_J \Delta G_J \rangle = (\sqrt{\rho_J} \Delta F_J | \sqrt{\rho_J} \Delta G_J) = \frac{1}{2} \text{Tr}(\rho_J \{ \Delta F_J, \Delta G_J \}) . \quad (92)$$

S_J may be interpreted as the subsystem entropy operator only if subsystem J is not correlated with the other subsystems, i.e., if ρ can be written as

$$\rho = \rho_J \otimes \rho_{\bar{J}} ; \quad (93)$$

then the subsystem entropy is defined and given by the nonlinear state functional of the reduced state operator,

$$\begin{aligned} s_J(\rho_J) &= \langle S_J \rangle = \text{Tr}(\rho_J S_J) = -k_B \text{Tr}(\rho_J \ln \rho_J) \\ &= \text{Tr}[\rho (S_J \otimes I_{\bar{J}})] = (\sqrt{\rho_J} | \sqrt{\rho_J} S_J) , \end{aligned} \quad (94)$$

$$S = S_J \otimes I_{\bar{J}} + I_J \otimes S_{\bar{J}} , \quad (95)$$

$$s(\rho) = s_J(\rho_J) + s_{\bar{J}}(\rho_{\bar{J}}) , \quad (96)$$

and we also have $(\Delta S)^J = \Delta S_J$.

When subsystem J is correlated, instead, its entropy is not defined; however, the functional

$$s^J(\rho) = \langle (S)^J \rangle = \text{Tr}[\rho_J(S)^J] = (\sqrt{\rho_J} | \sqrt{\rho_J}(S)^J) \quad (97)$$

may be interpreted as the subsystem's local perception of the overall-system entropy. Only when J is uncorrelated, $s^J(\rho) = s(\rho) = s_J(\rho_J) + s_{\bar{J}}(\rho_{\bar{J}})$.

The energy is defined for a subsystem J only if it is not interacting with the other subsystems, i.e., if H can be written as

$$H = H_J \otimes I_{\bar{J}} + I_J \otimes H_{\bar{J}} ; \quad (98)$$

then it is given by the mean-value state functional

$$e_J(\rho_J) = \langle H_J \rangle = \text{Tr}(\rho_J H_J) = (\sqrt{\rho_J} | \sqrt{\rho_J} H_J) , \quad (99)$$

and we also have $(\Delta H)^J = \Delta H_J$.

When subsystem J is interacting, instead, its energy is not defined; however the functional

$$e^J(\rho) = \langle (H)^J \rangle = \text{Tr}[\rho_J(H)^J] = (\sqrt{\rho_J} | \sqrt{\rho_J}(H)^J) \quad (100)$$

may be interpreted as the subsystem's local perception of the overall-system energy. Only when J is non-interacting, $e^J(\rho) = e(\rho) = e_J(\rho_J) + e_{\bar{J}}(\rho_{\bar{J}})$.

The number-of-particles-of- i -th-type of the overall system in state ρ and of each subsystem J are given by the mean-value state functionals $n_i(\rho) = \langle N_i \rangle = \text{Tr}(\rho N_i)$ and $n_{i,J}(\rho_J) = \langle N_{i,J} \rangle = \text{Tr}[\rho(N_{i,J} \otimes I_{\bar{J}})] = n_i^J(\rho) = \langle (N_{i,J} \otimes I_{\bar{J}})^J \rangle = \text{Tr}(\rho_J N_{i,J}) = (\sqrt{\rho_J} | \sqrt{\rho_J} N_{i,J})$, respectively, and from (80) we clearly have $n_i(\rho) = \sum_{J=1}^M n_{i,J}(\rho_J)$. Indeed, it is noteworthy that, for any ρ ,

$$(N_{i,J} \otimes I_{\bar{J}})^J = N_{i,J} . \quad (101)$$

For generality, we assume that the generators of the motion on \mathcal{H} are I , H and G_i , with $[G_i, H] = 0$ but not necessarily with the separated structure of the number operators. Moreover, for each state ρ and each constituent J , we denote by $\{R_{i,J}, i = 0, 1, 2, \dots, z_J(\rho)\}$ a set of hermitian operators in $\mathcal{L}(\mathcal{H})$ such that the operators in the set $\{\sqrt{\rho_J}(R_{i,J})^J\}$, where

$$(R_{i,J})^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}}) R_{i,J}] \quad (102)$$

are linearly independent and span the linear manifold generated by the operators $\sqrt{\rho_J} I_J$, $\sqrt{\rho_J}(H)^J$, $\sqrt{\rho_J}(G_i)^J$. If the latter operators are linearly independent, for subsystem J , then the set $\{R_{i,J}\}$ may be chosen to coincide with the generators of the motion. If they are not independent, then it could be a smaller subset (in which it is convenient, though not necessary, to maintain $R_{0,J} = I$ and, if possible, $R_{1,J} = H$). In any case, we call the operators in the set $\{R_{i,J}\}$ the (instantaneous) "generators of the motion of subsystem J ". The structure of the irreversible term $\hat{\mathbf{D}}_M$ is invariant under transformation from one set $\{R_{i,J}\}$ to any other $\{R'_{i,J}\}$ with the same defining properties.

For each instantaneous generator $R_{i,J}$ of subsystem J , we define the "local perception" mean functional

$$r_{i,J}^J(\rho) = \text{Tr}[\rho_J(R_{i,J})^J] = (\sqrt{\rho_J} | \sqrt{\rho_J}(R_{i,J})^J) . \quad (103)$$

We denote by

$$\mathcal{L}\{\sqrt{\rho_J}(R_{i,J})^J\} = \mathcal{L}\{\sqrt{\rho_J} I_J, \sqrt{\rho_J}(H)^J, \sqrt{\rho_J}(G_i)^J\} \quad (104)$$

the linear span of the operators $\{\sqrt{\rho_J}(R_{i,J})^J\}$ or, that is the same, the linear span of the operators $\sqrt{\rho_J} I_J$, $\sqrt{\rho_J}(H)^J$, $\sqrt{\rho_J}(G_i)^J$.

By definition of the set $\{R_{i,J}\}$, the Gram determinant

$$\begin{aligned} \Gamma(\{\sqrt{\rho_J}(R_{i,J})^J\}) &= \det[\{(\sqrt{\rho_J}(R_{i,J})^J | \sqrt{\rho_J} R_{j,J})^J\}] \\ &= \det[\{\langle \Delta R_{i,J} \Delta R_{j,J} \rangle^J\}] \end{aligned} \quad (105)$$

is always strictly positive.

The set $\{R_{iJ}\}$ can be conveniently chosen so that $\{\sqrt{\rho_J}(R_{iJ})^J\}$ is (instantaneously) an orthonormal set, in which case we denote it by $\{\sqrt{\rho_J}(A_{iJ})^J\}$ and

$$(\sqrt{\rho_J}(A_{iJ})^J | \sqrt{\rho_J}(A_{jJ})^J) = \delta_{ij} , \quad (106)$$

$$\Gamma_J(\{\sqrt{\rho_J}(A_{iJ})^J\}) = 1 . \quad (107)$$

11. The steepest-entropy-ascent ansatz for a composite system

Maintaining the validity of (3) and (18), we now assume

$$\sqrt{\rho} E_D = \sum_{J=1}^M \sqrt{\rho_J} E_{DJ} \otimes \rho_J , \quad (108)$$

as a first step to guarantee the strong separability condition (77) [see Appendix G for a discussion related to the form of (108)].

The second step is to make sure that E_{DJ} , which in general may be a function of the operators ρ , H and G_i on \mathcal{H} , reduces to a function of the operators ρ_J , H_J and G_{iJ} on \mathcal{H}^J only, whenever the constituent is, at the same time, uncorrelated ($\rho = \rho_J \otimes \rho_{\bar{J}}$), non-interacting ($H = H_J \otimes I_{\bar{J}} + I_J \otimes H_{\bar{J}}$) and not coupled through the non-Hamiltonian generators ($G_i = G_{iJ} \otimes I_{\bar{J}} + I_J \otimes G_{i\bar{J}}$).

To preserve the formal analogy with the notation for the indivisible system, we define the local “partial gradient” operators

$$\left[\frac{\partial r_{iJ}^J(\rho)}{\partial \sqrt{\rho_J}} \right]_{(R_{iJ})^J} = \sqrt{\rho_J}(R_{iJ})^J + (R_{iJ})^J \sqrt{\rho_J} , \quad (109)$$

$$\left[\frac{\partial s^J(\rho)}{\partial \sqrt{\rho_J}} \right]_{(S)^J} = 2\sqrt{\rho_J}(S)^J . \quad (110)$$

Now, it is easy to show that the structure of $d\rho/dt$ assumed with (3), (18) and (108) yields [37]

$$\frac{dr_{iJ}(\rho)}{dt} = \text{Tr} \left(\frac{d\rho}{dt} R_{iJ} \right) = 2 \sum_{J=1}^M \left(E_{DJ} | \sqrt{\rho_J}(R_{iJ})^J \right) , \quad (111)$$

$$\begin{aligned} \frac{ds(\rho)}{dt} &= -k_B \text{Tr} \left(\frac{d\rho}{dt} \right) - k_B \text{Tr} \left(\frac{d\rho}{dt} B \ln \rho \right) \\ &= \sum_{J=1}^M \left[-2k_B (E_{DJ} | \sqrt{\rho_J} I_J)_J + 2(E_{DJ} | \sqrt{\rho_J}(S)^J) \right] \\ &= \sum_{J=1}^M \left[-2k_B (\sqrt{\rho_J} I_J | E_{DJ}) + \left(\left[\frac{\partial s^J(\rho)}{\partial \sqrt{\rho_J}} \right]_{(S)^J} \middle| E_{DJ} \right) \right] . \end{aligned} \quad (112)$$

Finally, we assume that each E_{DJ} is: (A) orthogonal to $\mathcal{L}\{\sqrt{\rho_J}(R_{iJ})^J\}$, so that all the rates of change in (111) and the first term in the rate of entropy change in (112) are zero; and (B) in the direction of the local partial gradient of the “locally perceived” overall-system entropy functional, $s^J(\rho)$, i.e., we take

$$E_{DJ} = \frac{1}{4k_B \tau_J(\rho)} \left[\left[\frac{\partial s^J(\rho)}{\partial \sqrt{\rho_J}} \right]_{(S)^J} \right]_{\perp \mathcal{L}\{\sqrt{\rho_J}(R_{iJ})^J\}} = -\frac{1}{2\tau_J(\rho)} D_J , \quad (113)$$

where, similarly to what is done for the indivisible system,

$$D_J = \left[\sqrt{\rho_J}(B \ln \rho)^J \right]_{\perp \mathcal{L}\{\sqrt{\rho_J}(R_{iJ})^J\}} \quad (114a)$$

$$= \sqrt{\rho_J}(B \ln \rho)^J - \left[\sqrt{\rho_J}(B \ln \rho)^J \right]_{\mathcal{L}\{\sqrt{\rho_J}(R_{iJ})^J\}} \quad (114b)$$

$$= - \frac{\begin{vmatrix} \sqrt{\rho_J}(\Delta S)^J & \sqrt{\rho_J}(\Delta R_{1J})^J & \cdots & \sqrt{\rho_J}(\Delta R_{iJ})^J & \cdots \\ \langle \Delta S \Delta R_{1J} \rangle^J & \langle \Delta R_{1J} \Delta R_{1J} \rangle^J & \cdots & \langle \Delta R_{iJ} \Delta R_{1J} \rangle^J & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta S \Delta R_{iJ} \rangle^J & \langle \Delta R_{1J} \Delta R_{iJ} \rangle^J & \cdots & \langle \Delta R_{iJ} \Delta R_{iJ} \rangle^J & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{k_B \Gamma(\{\sqrt{\rho_J}(R_{iJ})^J\})}. \quad (114c)$$

Most of the results found for the single constituent extend to the composite system in a straightforward way. In particular, using the properties of determinants it is easy to verify that

$$(E_{DJ}|\sqrt{\rho_J}) = \text{Tr}(\sqrt{\rho_J}E_{DJ}^\dagger + E_{DJ}^\dagger\sqrt{\rho_J}) = 0 \quad (115)$$

and that the mean value of each R_{iJ} is independently conserved by each subsystem, i.e., $(E_{DJ}|\sqrt{\rho_J}(R_{iJ}^J) = 0$, and therefore $\text{Tr}(\rho I)$, $\text{Tr}(\rho H)$, and the $\text{Tr}(\rho G_i)$'s are time invariant.

In general, by virtue of (19), (75), (108), and (115), the rate of change of the reduced state operator of subsystem J is given by the equation

$$\frac{d\rho_J}{dt} = -\frac{i}{\hbar}[H_J, \rho_J] - \frac{i}{\hbar}\text{Tr}_J([V, \rho]) + \left(\frac{D\rho}{Dt}\right)^J \quad (116)$$

where we defined

$$\left(\frac{D\rho}{Dt}\right)^J = \text{Tr}_J\left(\frac{D\rho}{Dt}\right) = \sqrt{\rho_J}E_{DJ}^\dagger + E_{DJ}^\dagger\sqrt{\rho_J}. \quad (117)$$

Indeed, in general, we have

$$\frac{D\rho}{Dt} = \frac{d\rho}{dt} + \frac{i}{\hbar}[H, \rho] = \sum_{J=1}^M \left(\frac{D\rho}{Dt}\right)^J \otimes \rho_J. \quad (118)$$

The rate of entropy change is given by the relations

$$\frac{ds(\rho)}{dt} = \sum_{J=1}^M \frac{k_B}{\tau_J(\rho)} (D_J|D_J) \quad (119a)$$

$$= \sum_{J=1}^M 4k_B \tau_J(\rho) (E_{DJ}|E_{DJ}) \quad (119b)$$

$$= \sum_{J=1}^M \frac{1}{k_B \tau_J(\rho)} \frac{\Gamma(\sqrt{\rho_J}(S)^J, \{\sqrt{\rho_J}(R_{iJ})^J\})}{\Gamma(\{\sqrt{\rho_J}(R_{iJ})^J\})}. \quad (119c)$$

The dynamics reduces to the Schrödinger-von Neumann unitary Hamiltonian dynamics when

$$\sqrt{\rho_J}(B \ln \rho)^J = \sqrt{\rho_J}(C)^J \quad \text{with} \quad C = \sum_i \lambda_{iJ} R_{iJ}, \quad (120)$$

for each J and, therefore, the state is nondissipative {equilibrium if $[B, H] = 0$, limit cycle if $[B, H] \neq 0$, including the case of pure-state standard QM when $\text{Tr}(B) = 1$ }.

The maximum entropy thermodynamic equilibrium states are given by (32).

Onsager's reciprocity relations follow again from (38) for the operator $B \ln \rho$. Eqs. (53) and (56) are still valid [of course, with $\hat{\mathbf{D}}_M$ in (52) instead of $\hat{\mathbf{D}}_1$], with the dissipative conductivities given by

$$L_{ij}(\rho) = L_{ji}(\rho) = \sum_{J=1}^M L_{ij}^J(\rho), \quad (121a)$$

$$L_{ij}^J(\rho) = L_{ji}^J(\rho) = \frac{\begin{vmatrix} \langle \Delta X_i \Delta X_j \rangle^J & \langle \Delta R_1 \Delta X_j \rangle^J & \cdots & \langle \Delta R_k \Delta X_j \rangle^J & \cdots \\ \langle \Delta X_i \Delta R_1 \rangle^J & \langle \Delta R_1 \Delta R_1 \rangle^J & \cdots & \langle \Delta R_k \Delta R_1 \rangle^J & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta X_i \Delta R_k \rangle^J & \langle \Delta R_1 \Delta R_k \rangle^J & \cdots & \langle \Delta R_k \Delta R_k \rangle^J & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{k_B \tau_J(\rho) \Gamma(\{\sqrt{\rho_J}(R_{iJ})^J\})}. \quad (121b)$$

Callen's fluctuation-dissipation relations, implied by the explicit structure [(121)] of the Onsager dissipative conductivities, are greatly simplified if we choose the orthonormal set $\{\sqrt{\rho_J}(A_{iJ})^J\}$ instead of $\{\sqrt{\rho_J}(R_{iJ})^J\}$ and the set $\{\sqrt{\rho_J}(X_{jJ})^J\}$ to be an orthogonal extension of $\{\sqrt{\rho_J}(A_{iJ})^J\}$; then,

$$L_{ij}^J(\rho) = \frac{1}{k_B \tau_J(\rho)} \langle \Delta X_i \Delta X_j \rangle^J. \quad (122)$$

The assumption about the time-energy Heisenberg uncertainty relation in section 7 can be extended as well. We assume that each E_{DJ} gives rise to a characteristic time $\tau_{DJ}(\rho)$ defined by (see Appendix C)

$$\frac{1}{\tau_{DJ}(\rho)^2} = 4 \langle E_{DJ} | E_{DJ} \rangle, \quad (123)$$

which should independently satisfy the uncertainty relation

$$\tau_{DJ}(\rho)^2 \langle \Delta H \Delta H \rangle^J \geq \hbar^2 / 4. \quad (124)$$

Therefore, using (113) and (114), we obtain the lower bounds to the internal relaxation times,

$$\tau_J(\rho)^2 \geq \frac{\hbar^2}{4k_B^2} \frac{\Gamma(\sqrt{\rho_J}(S)^J, \{\sqrt{\rho_J}(R_{iJ})^J\})}{\langle \Delta H \Delta H \rangle^J \Gamma(\{\sqrt{\rho_J}(R_{iJ})^J\})} = \frac{\hbar^2 (D_J | D_J)}{4 \langle \Delta H \Delta H \rangle^J} \quad (125)$$

or, using, (119) and (56),

$$\tau_J(\rho) \geq \frac{\hbar^2}{4k_B \langle \Delta H \Delta H \rangle^J} \sum_i \sum_j f_i f_j L_{ij}^J(\rho), \quad (126)$$

and the upper bound to the entropy generation rate

$$\frac{ds(\rho)}{dt} \leq \sum_{J=1}^M \frac{2}{\hbar} \sqrt{\frac{\langle \Delta H \Delta H \rangle^J \Gamma(\sqrt{\rho_J}(S)^J, \{\sqrt{\rho_J}(R_{iJ})^J\})}{\Gamma(\{\sqrt{\rho_J}(R_{iJ})^J\})}}. \quad (127)$$

Taking strict equalities in each of (125) yields the maximum entropy generation rate compatible with the time-energy uncertainty relations, and corresponds to a possible "extreme" closure ansatz.

The variational formulation can be found, after assuming the structure of (108), by solving the constrained maximization problem

$$\max \frac{ds}{dt}(\{E_{DJ}\}) \quad (128a)$$

$$\text{subject to } \frac{dr_{iJ}}{dt}(\{E_{DJ}\}) = \dot{r}_{iJ} \text{ and } (E_{DJ}|E_{DJ}) = \frac{1}{4\tau_{DJ}^2}, \quad (128b)$$

where \dot{r}_{iJ} and τ_{DJ}^2 are given real functionals of ρ . By virtue of (111) and (112), the necessary solving conditions in terms of Lagrange multipliers for each E_{DJ} become

$$\left[\frac{\partial s^J(\rho)}{\partial \sqrt{\rho^J}} \right]_{(S)^J} - 2 \sum_i \lambda_i^J \sqrt{\rho^J} (R_{iJ})^J - \lambda_0^J E_{DJ} = 0, \quad (129)$$

clearly verified by the E_{DJ} 's given in (113) and (114).

If two subsystems A and B are non-interacting but in correlated states, the reduced state operators obey the equations

$$\frac{d\rho_A}{dt} = -\frac{i}{\hbar} [H_A, \rho_A] - \sum_{\substack{J=1 \\ J \in A}}^M \frac{1}{2\tau_J(\rho)} [\sqrt{\rho^J} D_J + D_J^\dagger \sqrt{\rho^J}] \otimes (\rho_A)_{\bar{J}}, \quad (130a)$$

$$\frac{d\rho_B}{dt} = -\frac{i}{\hbar} [H_B, \rho_B] - \sum_{\substack{J=1 \\ J \in B}}^M \frac{1}{2\tau_J(\rho)} [\sqrt{\rho^J} D_J + D_J^\dagger \sqrt{\rho^J}] \otimes (\rho_B)_{\bar{J}}, \quad (130b)$$

where $(\rho_A)_{\bar{J}} = \text{Tr}_J(\rho_A)$ and $(\rho_B)_{\bar{J}} = \text{Tr}_J(\rho_B)$.

The strong separability conditions (77) are satisfied provided the internal-relaxation-time functionals are either all constants or satisfy the following set of nontrivial conditions,

$$\begin{aligned} & \tau_J(\rho_A \otimes \rho_B, H_A \otimes I_B + I_A \otimes H_B, G_{iA} \otimes I_B + I_A \otimes G_{iB}) \\ &= \begin{cases} \tau_J(\rho_A, H_A, G_{iA}) & \text{for } J \in A \\ \tau_J(\rho_B, H_B, G_{iB}) & \text{for } J \in B \end{cases} \quad \text{for any } \rho_A \text{ and } \rho_B, \end{aligned} \quad (131a)$$

$$\begin{aligned} & \tau_J(\rho, H_A \otimes I_B + I_A \otimes H_B, G_{iA} \otimes I_B + I_A \otimes G_{iB}) \\ &= \begin{cases} \tau_J'(\rho, H_A, G_{iA}) & \text{for } J \in A \\ \tau_J'(\rho, H_B, G_{iB}) & \text{for } J \in B \end{cases} \quad \text{for any } \rho. \end{aligned} \quad (131b)$$

It is noteworthy that Conditions (131) are satisfied by the maximal-entropy-generation-rate ansatz, i.e., if we assume that each $\tau_J(\rho)$ is given by (125) with strict equality. Indeed, if A and B are noninteracting, the structure [114c] of each operator D_J with $J \in A$ is such that any dependence on H_B cancels out, moreover $\langle \Delta H \Delta H \rangle^J = \langle \Delta H_A \Delta H_A \rangle^J$. Thus, any dependence on H_B cancels out in (11a) and, similarly, any dependence on H_A cancels out in (11b).

It is interesting, however, that $d\rho_A/dt$ in general may depend not only on the ‘‘local’’ (reduced) state operator ρ_A but also on the overall state ρ through the operators $(B \ln \rho)^J$ (with $J \in A$), thus determining a collective-behavior effect on the local dynamics originating from existing correlations. In fact, operators D_J are in terms of $(\Delta S)^J$ which may differ, when the subsystems are correlated, from operators $(\Delta S_A)^J$. In other words, the lack of interactions between two subsystems does guarantee that the energy of each subsystem is defined and conserved [(78)] and that the reduced dynamics of each subsystem is local, in the sense of independent of the Hamiltonian operator (and the other generators) of the other subsystem, but does not necessarily imply that each subsystem evolves independently of existing correlations with the other subsystem.

Regarding the time evolution of correlations, in [11] we defined the correlation functional between two subsystems A and B ,

$$\sigma_{AB}(\rho) = \text{Tr}(\rho \ln \rho) - \text{Tr}_A(\rho_A \ln \rho_A) - \text{Tr}_B(\rho_B \ln \rho_B), \quad (132)$$

which is nonnegative definite in general, and zero only if $\rho = \rho_A \otimes \rho_B$. The rate of change of the correlation can be written as

$$\frac{d\sigma_{AB}(\rho)}{dt} = \dot{\sigma}_{AB|H} - \dot{\sigma}_{AB|D} . \quad (133)$$

Based on our understanding of the equation of motion, we conjectured that $\dot{\sigma}_{AB|D}$ should always be nonnegative, if it is true that the irreversible term can only destroy correlations between subsystems, but cannot create them. However, this conjecture remains to be proved. The corresponding entropy inequality to our knowledge has not yet been studied.

12. Conclusions

Based on unpublished geometrical reasoning [10], on the ansatz that a broader quantum kinematics may unite mechanics and thermodynamics [7, 19], and on the ansatz of a maximal entropy generation quantum dynamics may entail and extend the traditional Schrödinger–von Neumann unitary dynamics, we rederived most previous results in [10, 11, 13, 14, 15, 16] on the well-behaved nonlinear equation of motion proposed by the present author in his 1981 doctoral thesis for quantum thermodynamics, which entails the second law and nonequilibrium steepest-entropy-ascent dynamics with Onsager’s reciprocity and Callen’s fluctuation-dissipation relations.

Together with the variational principle formulation derived in [3] and the observation in [7, 9] that only the functional $-k_B \text{Tr}(\rho \ln \rho)$ can represent the physical entropy, we may conclude that all the results so far confirm that our equation of motion has all the necessary features to provide a self-consistent and conceptually-sound resolution of the century-old dilemma on the nature of entropy and irreversibility, alternative to Boltzmann’s statistical approach and valid also for systems with few degrees of freedom.

The nonlinear dynamics encompasses within a unified framework all the successful results of quantum mechanics, equilibrium and nonequilibrium thermodynamics. It also holds the promise to provide a fundamental framework within which to address the currently unexplained evidence on loss of quantum coherence, to design new fundamental experiments, to examine new applications on the lines of those developed in [3, 15, 20], and to further investigate the dependence of the internal-relaxation-time functional on the state operator and physical constants, as well as possibly verify the ansatz proposed in this paper by which each indivisible subsystem follows the direction of steepest perceived entropy ascent at the highest rate compatible with the time–energy uncertainty principle.

The equation of motion satisfies the set of conditions discussed in Appendix A and, therefore, preserves most of the traditional conceptual keystones of physical thought, including a strongest form of the non-relativistic principle of causality, by which future states of a strictly isolated system should unfold deterministically from initial states along smooth unique trajectories in state domain defined for all times (future as well as past [38]). Interestingly, while the maximum entropy states are attractors in forward time, the unitary-solutions boundary limit cycles of standard quantum mechanics are attractors in backward time.

As pointed out by Onsager and Machlup [23], the fluctuation-dissipation relations cannot be derived in any rigorous way from the traditional Hamiltonian dynamical principles, unless these are complemented by some additional postulate closely related to the additional principles, assumptions, or approximations needed to derive the Onsager reciprocity relations. This is sometimes referred to as the irreversibility paradox. In other words, in order to infer any feature of irreversibility (including its very existence) from the irreducibly reversible dynamical principle of standard Hamiltonian mechanics, we must complement it with some additional postulate that seems to contradict it.

Within our nonlinear quantum (thermo)dynamics based on (1) and (2) the paradox is resolved. The augmented state domain ansatz broadens the set of conceivable states but includes the standard pure states, and the nonlinear equation of motion describes irreversible time evolutions and entails reciprocity and fluctuation-dissipation relations, but maintains the standard unitary dynamics of pure states. In fact, the proof emerges not from the Hamiltonian

term of the equation of motion but from the irreversible, maximum entropy production term and is, thus, accomplished without the aid of the usual empirical and heuristic assumptions (microscopic reversibility and small deviations from stable equilibrium).

Finally, from the Heisenberg time–energy uncertainty principle we derived a plausible lower bound for the internal-relaxation-time functionals from which follows an upper bound for the rate of entropy generation. Consequently, we proposed a rather extreme but physically intriguing maximal-entropy-generation-rate ansatz, by which each indivisible subsystem follows the direction of steepest perceived entropy ascent at the highest rate compatible with the time–energy uncertainty principle. If this ansatz is experimentally verified, the nonlinear dynamics is complete and self-consistent, with no need of new physical constants.

Subject, of course, to experimental and further theoretical validation, this extreme ansatz represents a possible closure of the original nonlinear dynamics with no need of new physical constants. Physically, it would imply for example that energy is spontaneously redistributed among the initially occupied energy levels of the system, at the fastest rate compatible with (a) the time–energy uncertainty limitations, (b) the system structure, and (c) the energy exchange rates among subsystems (as driven by the usual interaction terms in the Hamiltonian operator through the usual unitary-dynamics term in the equation of motion).

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Appendix A. Criteria for a general (nonlinear) quantum dynamics compatible with thermodynamics

Within a quantum theory that accepts the augmented set of true quantum states described by state operators ρ without the restriction $\rho^2 = \rho$, and a nonlinear dynamical law for a strictly isolated system, the following demanding set of conditions should be satisfied in order for the theory to be compatible or, better, imply the second law of thermodynamics without contradicting the fundamental results of standard quantum mechanics (QM). Obviously these are the criteria we followed in designing (1) and (2), and discussed at length in [13, 18].

Conditions 6, 7 and 8 are closely related to the condition recently referred to as strong separability [2]. We also added a condition on correlations and locality to reflect the need to avoid, and possibly resolve, physical inconsistencies related to nonlocality issues, as well as a strong causality condition that is nontrivial and quite demanding both from the conceptual and the technical mathematical points of view.

Certainly, when viewed from different perspectives — e.g., different physical interpretations of the augmented state domain $\rho^2 \neq \rho$ ansatz, of the role of the nonlinear extension of the Schrödinger equation of motion, of the Shannon-von Neumann entropy functional $-k_B \text{Tr}(\rho \ln \rho)$ versus other nonextensive functionals, of the role of the system's environment and the measuring apparatus, and so on — some authors might view this set of conditions as too strong in many respects. Nevertheless, our equation of motion demonstrates that at least a satisfactory dynamics exists which satisfies all such conditions and, in our view, features a number of intriguing, unifying and far-reaching implications.

1. Causality. Forward and backward in time

We consider the set \mathcal{P} of all linear, hermitian, nonnegative-definite, unit-trace operators ρ on the standard QM Hilbert space \mathcal{H} associated with the strictly isolated system[36]. Every

solution of the equation of motion, i.e., every trajectory $u(t, \rho)$ passing at time $t = 0$ through state ρ in \mathcal{P} , should lie entirely in \mathcal{P} for all times t , $-\infty < t < +\infty$.

2. Conservation of energy and number of particles

Since the system is isolated, the value of the energy functional $e(\rho) = \text{Tr}(\rho H)$, where H is the standard QM Hamiltonian operator, must remain invariant along every trajectory. If \mathcal{H} is the Fock space of an isolated system consisting of M types of elementary constituents (e.g., atoms and molecules if chemical and nuclear reactions are inhibited; or atomic nuclei and electrons for modelling chemical reactions) each with a number operator N_i ($[H, N_i] = 0$ and $[N_i, N_j] = 0$), then also the value of each number-of-constituents functional $n_i(\rho) = \text{Tr}(\rho N_i)$ must remain invariant along every trajectory. Depending on the type of system, there may be other time-invariant functionals, e.g., the total momentum components $p_j(\rho) = \text{Tr}(\rho P_j)$, with $j = x, y, z$, for a free particle (in which case Galileian invariance must also be verified, for $[H, P_j] = 0$ and $[P_i, P_j] = 0$). In what follows, we denote by $g_i(\rho) = \text{Tr}(\rho G_i)$ the set of non-Hamiltonian time-invariant functionals, if any, with $[H, G_i] = 0$ and $[G_i, G_j] = 0$ (clearly, H and the G_i 's have a common eigenbasis that we denote by $\{|\psi_\ell\rangle\}$).

3. Standard QM unitary evolution of pure ($\rho^2 = \rho$) states

The unitary time evolution of the states of QM according to the Schrödinger equation of motion must be compatible with the more general dynamical law. These trajectories, passing through any state ρ such that $\rho^2 = \rho$ and entirely contained in the state domain of Quantum Mechanics, must be solutions also of the more general dynamical law. In view of the fact that the states of QM are the extreme points of the augmented state domain \mathcal{P} , the trajectories of QM must be boundary solutions (limit cycles) of the dynamical law.

If the complete dynamics preserves the feature of uniqueness of solutions throughout the state domain \mathcal{P} , then pure states can only evolve according to the Schrödinger equation of motion and, therefore, $\dot{\mathbf{D}}_M(\rho, H, G_i, \dots) = 0$ when $\rho^2 = \rho$. This feature may be responsible for hiding the presence of deviations from QM in experiments where the isolated system is prepared in a pure state. It also implies that no trajectory can enter or leave the state domain of QM. Thus, by continuity, there must be trajectories that approach indefinitely these boundary solutions (of course, this can only happen backward in time, as $t \rightarrow -\infty$, for otherwise the entropy of the isolated system would decrease in forward time).

4. Entropy nondecrease. Irreversibility

The principle of nondecrease of entropy for an isolated system must be satisfied, i.e., the rate of change of the entropy functional $-k_B \text{Tr}(\rho \ln \rho)$ must be nonnegative along every trajectory, $-k_B \text{Tr}[u(t, \rho) \ln u(t, \rho)] \geq -k_B \text{Tr}(\rho \ln \rho)$.

5. Stability of the thermodynamic equilibrium states. Second law

A state operator ρ of the isolated system represents an equilibrium state if $d\rho/dt = 0$. For each given set of feasible values of the energy functional $e(\rho)$ and the number-of-particle functionals $n_i(\rho)$ (i.e., the functionals that must remain invariant according to Condition 2 above), among all the equilibrium states that the dynamical law may admit there must be one and only one which is globally stable (definition and discussion in Appendix B). This stable equilibrium state must represent the corresponding state of equilibrium thermodynamics and, therefore, must be of the form given by (32). All the other equilibrium states that the dynamical law may admit must not be globally stable.

6. Non-interacting subsystems. Separate energy conservation

For an isolated system composed of two distinguishable subsystems A and B with associated Hilbert spaces \mathcal{H}^A and \mathcal{H}^B , so that the Hilbert space of the system is $\mathcal{H} = \mathcal{H}^A \otimes \mathcal{H}^B$, if the

two subsystems are non-interacting, i.e., the Hamiltonian operator $H = H_A \otimes I_B + I_A \otimes H_B$, then the functionals $\text{Tr}[(H_A \otimes I_B)\rho] = \text{Tr}_A(H_A \rho_A)$ and $\text{Tr}[(I_A \otimes H_B)\rho] = \text{Tr}_B(H_B \rho_B)$ represent the energies of the two subsystems and must remain invariant along every trajectory, even if the states of A and B are correlated, i.e., even if $\rho \neq \rho_A \otimes \rho_B$. Of course, $\rho_A = \text{Tr}_B(\rho)$, $\rho_B = \text{Tr}_A(\rho)$, Tr_B denotes the partial trace over \mathcal{H}^B and Tr_A the partial trace over \mathcal{H}^A .

7. Independent states. Weak separability. Separate entropy nondecrease

Two distinguishable subsystems A and B are in independent states if the state operator $\rho = \rho_A \otimes \rho_B$, so that the entropy operator $S = -k_B B \ln \rho = S_A \otimes I_B + I_A \otimes S_B = -k_B [B_A \ln \rho_A \otimes I_B + I_A \otimes B_B \ln \rho_B]$. For permanently non-interacting subsystems, every trajectory passing through a state in which the subsystems are in independent states must maintain the subsystems in independent states along the entire trajectory. When two uncorrelated systems do not interact with each other, each must evolve in time independently of the other.

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

8. Correlations and locality. Strong separability

Two non-interacting subsystems A and B initially in correlated states (possibly due to a previous interaction that has then been turned off) should each proceed in time towards less correlated states or, at least, maintain the same level of quantum entanglement. The generation of quantum entanglement between interacting subsystems should emerge only through the Schrödinger-von Neumann term $-i[H, \rho]/\hbar$ of the equation of motion, whereas the other terms, that might entail loss of correlations between subsystems, must not be able to create them. This condition is perhaps too strong and its validity for our equation is still only conjectural. In any case, the dynamics should not generate locality problems, i.e., faster-than-light communication between noninteracting subsystems, even if in entangled or correlated states. In other words, when subsystem A is not interacting with subsystem B , it should never be possible to influence the local observables of A by acting only on the interactions within B , such as switching on and off parameters or measurement devices within B . This does not mean that existing 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, we see no physical reason to request that two different states ρ and ρ' such that $\rho'_A = \rho_A$ should evolve in such a way that $d\rho'_A/dt = d\rho_A/dt$ whenever A is isolated (but not uncorrelated) from the rest of the overall system. For example, state ρ' could be the maximum entropy stable equilibrium state (and, therefore, $\rho' = \rho'_A \otimes \rho'_B$, $d\rho'/dt = 0$) whereas in state ρ subsystems A and B could be correlated and evolving in time towards the stable equilibrium state or ρ could even be a pure entangled state evolving along a unitary trajectory according to Condition 3 above, and therefore it would never reach stable equilibrium.

Appendix B. Lyapunov stability and thermodynamic stability

The condition concerning stability of the thermodynamic equilibrium states is extremely restrictive and requires further discussion.

In order to implement Condition 5 in Appendix A, we need to establish the relation between the notion of stability implied by the second law of thermodynamics [32, 33] and the mathematical concept of stability. An equilibrium state is stable, in the sense required by the second law, if it can be altered to a different state only by interactions that leave net effects in the state of the environment. We call this notion of stability *global stability*. The notion of stability according to Lyapunov is called *local stability*.

We denote the trajectories generated by the dynamical law on our state domain by $u(t, \rho)$, i.e., $u(t, \rho)$ denotes the state at time t along the trajectory that at time $t = 0$ passes through

state ρ . A state ρ_e is an equilibrium state if and only if $u(t, \rho_e) = \rho_e$ for all times t . An equilibrium state ρ_e is *locally stable* (according to Lyapunov) if and only if for every $\epsilon > 0$ there is a $\delta(\epsilon) > 0$ such that $d(\rho, \rho_e) < \delta(\epsilon)$ implies $d(u(t, \rho), \rho_e) < \epsilon$ for all $t > 0$ and every ρ , i.e., such that every trajectory that passes within the distance $\delta(\epsilon)$ from state ρ_e proceeds in time without ever exceeding the distance ϵ from ρ_e . Conversely, an equilibrium state ρ_e is unstable if and only if it is not locally stable, i.e., there is an $\epsilon > 0$ such that for every $\delta > 0$ there is a trajectory passing within distance δ from ρ_e and reaching at some later time farther than the distance ϵ from ρ_e .

The Lyapunov concept of instability of equilibrium is clearly equivalent to that of instability stated in thermodynamics according to which an equilibrium state is unstable if, upon experiencing a minute and short lived influence by some system in the environment (i.e., just enough to take it from state ρ_e to a neighbouring state at infinitesimal distance δ), proceeds from then on spontaneously to a sequence of entirely different states (i.e., farther than some finite distance ϵ).

It follows that the concept of stability in thermodynamics implies that of Lyapunov local stability. However, it is stronger because it also excludes the concept of *metastability*. Namely, the states of equilibrium thermodynamics are *global* stable equilibrium states in the sense that not only they are locally stable but they cannot be altered to entirely different states even by means of interactions which leave temporary but finite effects in the environment. Mathematically, the concept of metastability can be defined as follows. An equilibrium state ρ_e is *metastable* if and only if it is locally stable but there is an $\eta > 0$ and an $\epsilon > 0$ such that for every $\delta > 0$ there is a trajectory $u(t, \rho)$ passing at $t = 0$ between distance η and $\eta + \delta$ from ρ_e , $\eta < d(u(0, \rho), \rho_e) < \eta + \delta$, and reaching at some later time $t > 0$ a distance farther than $\eta + \epsilon$, $d(u(t, \rho), \rho_e) \geq \eta + \epsilon$. Thus, the concept of global stability implied by the second law is as follows. An equilibrium state ρ_e is *globally stable* if for every $\eta > 0$ and every $\epsilon > 0$ there is a $\delta(\epsilon, \eta) > 0$ such that every trajectory $u(t, \rho)$ with $\eta < d(u(0, \rho), \rho_e) < \eta + \delta(\epsilon, \eta)$, i.e., passing at time $t = 0$ between distance η and $\eta + \delta$ from ρ_e , remains within $d(u(t, \rho), \rho_e) < \eta + \epsilon$ for every $t > 0$, i.e., proceeds in time without ever exceeding the distance $\eta + \epsilon$.

The second law requires that for each set of values of the invariants $\text{Tr}(\rho H)$ and $\text{Tr}(\rho G_i)$ (as many G_i 's as required by the structure of the system), and of the parameters embedded in the Hilbert space \mathcal{H} and the Hamiltonian H describing the external forces (such as the size of a container), there is one and only one globally stable equilibrium state. Thus, the dynamical law may admit many equilibrium states that all share the same values of the invariants and the parameters, but among all these only one is globally stable, i.e., all the other equilibrium states are either unstable or metastable.

Interestingly, we may use this condition to show that a unitary (Hamiltonian) dynamical law would be inconsistent with the second-law stability requirement. A unitary dynamical law in the augmented kinematics would be expressed by an equation of motion $i\hbar\dot{\rho} = [H, \rho]$ with trajectories $u(t, \rho) = U(t)\rho U^{-1}(t)$ with $U(t) = \exp(-itH/\hbar)$. Such a dynamical law would admit as equilibrium states all the states ρ_e such that $\rho_e H = H\rho_e$. Of these states there are more than just one for each set of values of the invariants. With respect to the metric $d(\rho_1, \rho_2) = \text{Tr}|\rho_1 - \rho_2|$, it is easy to show that every trajectory $u(t, \rho)$ would be equidistant from any given equilibrium state ρ_e , i.e., $d(u(t, \rho), \rho_e) = d(u(0, \rho), \rho_e)$ for all t and all ρ . Therefore, all the equilibrium states would be globally stable and there would be more than just one for each set of values of the invariants, thus violating the second-law requirement.

The entropy functional $-k_B \text{Tr}(\rho \ln \rho)$ plays a useful role in proving the stability of the states of equilibrium thermodynamics [(32)] provided that the dynamical law guarantees that $-k_B \text{Tr}[u(t, \rho) \ln u(t, \rho)] \geq -k_B \text{Tr}(\rho \ln \rho)$ for every trajectory, i.e., provided Condition 4 above is satisfied. The proof of this is nontrivial and is given in [32] where, however, we also show that the entropy functional is not a Lyapunov function, even if, in a strict sense that depends on the continuity and the conditional stability of the states of equilibrium thermodynamics, it does provide a criterion for the stability of these states. Anyway, even if the entropy were a Lyapunov function, this would suffice only to guarantee the local stability of the states of equilibrium thermodynamics but not to guarantee, as required by the second law, the

instability or metastability of all the other equilibrium states.

Appendix C. Characteristic times

Using (3), the rate of change of the mean functional $f(\rho) = \text{Tr}(\rho F)$ may be written as

$$\frac{df(\rho)}{dt} = \text{Tr} \left(\frac{d\rho}{dt} F \right) = 2(\sqrt{\rho} F | E) . \quad (\text{C.1})$$

For the Schrödinger–von Neumann evolution, the characteristic time of change of $f(\rho)$ may be defined as [39]

$$\frac{1}{\tau_{FH}^2} = \frac{[df(\rho)/dt]^2}{\langle \Delta F \Delta F \rangle} = \frac{4(\sqrt{\rho} \Delta F | E_H)^2}{\langle \Delta F \Delta F \rangle} . \quad (\text{C.2})$$

Because operators $\sqrt{\rho} \Delta F / \sqrt{\langle \Delta F \Delta F \rangle}$ are unit norm, in the sense that $(\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta F) / \langle \Delta F \Delta F \rangle = 1$, it follows that the characteristic times τ_{FH} are bounded by the value attained for an operator F such that $\sqrt{\rho} \Delta F$ is in the same direction as E_H , i.e., such that

$$\frac{\sqrt{\rho} \Delta F}{\sqrt{\langle \Delta F \Delta F \rangle}} = \frac{E_H}{\sqrt{\langle E_H | E_H \rangle}} . \quad (\text{C.3})$$

Therefore,

$$\frac{1}{\tau_{FH}^2} \leq 4(E_H | E_H) = \frac{1}{\tau_H^2} . \quad (\text{C.4})$$

For this reason, in (14) we take τ_H equal to the lower bound of the τ_{FH} 's.

By analogy, but considering separately the contribution of each subsystem to the overall-system dynamics embedded in our nonlinear dynamics, we define the characteristic time of the irreversible part of the rate of change of the mean functional $f(\rho) = \text{Tr}(\rho F)$ due to the J -th constituent subsystem as

$$\frac{1}{\tau_{FDJ}^2} = \frac{[Df(\rho)/Dt]_J^2}{\langle \Delta F \Delta F \rangle^J} = \frac{4(\sqrt{\rho_J} (\Delta F)^J | E_{DJ})^2}{\langle \Delta F \Delta F \rangle^J} . \quad (\text{C.5})$$

Again, because operators $\sqrt{\rho_J} (\Delta F)^J / \sqrt{\langle \Delta F \Delta F \rangle^J}$ are unit norm, in the sense that $(\sqrt{\rho_J} (\Delta F)^J | \sqrt{\rho_J} (\Delta F)^J) / \langle \Delta F \Delta F \rangle^J = 1$, it follows that the characteristic times τ_{FDJ} are bounded by the value attained for an operator F such that $\sqrt{\rho_J} (\Delta F)^J$ is in the same direction as E_{DJ} , i.e., such that

$$\frac{\sqrt{\rho_J} (\Delta F)^J}{\sqrt{\langle \Delta F \Delta F \rangle^J}} = \frac{E_{DJ}}{\sqrt{\langle E_{DJ} | E_{DJ} \rangle}} . \quad (\text{C.6})$$

Therefore,

$$\frac{1}{\tau_{FDJ}^2} \leq 4(E_{DJ} | E_{DJ}) = \frac{1}{\tau_{DJ}^2} . \quad (\text{C.7})$$

For this reason, in (62) and (123) we take τ_D and τ_{DJ} equal to the respective lower bounds of the τ_{FDJ} 's.

Appendix D. Special form of the equation of motion

If, for a given state operator ρ , we construct the set $\{\sqrt{\rho}X_j\}$ so as to be an orthogonal extension of the orthonormal subset $\{\sqrt{\rho}A_i\}$, i.e., with $X_i = A_i$ for $i \leq a$ and $(\sqrt{\rho}X_i|\sqrt{\rho}X_j) = \delta_{ij}$ for all i and j , then $D = -\sum_{j>a} f_j \sqrt{\rho}X_j$ [(45)] and the one-constituent equation of motion reduces to the (only apparently linear) form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2\tau(\rho)} \sum_{j>a} f_j(\rho) \{X_j(\rho), \rho\}, \quad (\text{D.1})$$

where the dependences of f_j , X_j and τ on ρ are evidenced in order to emphasize the nonlinearity.

For such special choice of the X_j 's, assuming $X_1 = I$, we have $x_1(\rho) = \text{Tr}(\rho) = 1$, $x_{i \neq 1}(\rho) = \text{Tr}(\rho X_{i \neq 1}) = 0$, $\langle \Delta X_1 \Delta X_i \rangle = 0$, $\langle \Delta X_{i \neq 1} \Delta X_{j \neq 1} \rangle = \delta_{ij}$, $L_{ij}(\rho) = 0$ and $Dx_i(\rho)/Dt = 0$ for i or $j \leq a$, $L_{ij}(\rho) = \delta_{ij}/\tau(\rho)$ and $Dx_i(\rho)/Dt = f_i(\rho)/\tau(\rho)$ for i and $j > a$, so that

$$\frac{ds(\rho)}{dt} = \frac{k_B}{\tau(\rho)} \sum_{k>a} f_k(\rho)^2, \quad (\text{D.2})$$

$$\tau(\rho)|_{\min} = \frac{\hbar}{2\langle \Delta H \Delta H \rangle} \sqrt{\sum_{k>a} f_k(\rho)^2}, \quad (\text{D.3})$$

$$\left. \frac{ds(\rho)}{dt} \right|_{\max} = \frac{2k_B}{\hbar} \sqrt{\langle \Delta H \Delta H \rangle} \sqrt{\sum_{k>a} f_k(\rho)^2}, \quad (\text{D.4})$$

where in the last two equations we made use of (26), (65) and (66) with strict equality.

In view of the dependence of the X_j 's on ρ and, therefore, on time, the apparently simple form of (D.1) may not be as useful as it seems.

Appendix E. Extension to time-varying rates of the generators of the motion

For the purposes of quantum thermodynamics, in our view the irreversible part of the equation of motion should not account for rates of change of the mean values of the generators of the motion other than through the Hamiltonian term, consistently with all the results of standard QM.

Nevertheless, the mathematical extension of (1) and (2) to (artificially) imposed rates $\dot{r}_i \neq 0$ (arbitrarily specified as functions of time) is straightforward and may be useful in modeling applications or other frameworks [6, 17]. It does emerge naturally from the maximization problem (47); it does so, however, implicitly, through substitution of (70) back into the constraint Eqs. (68b).

The explicit form in terms of projections and, therefore, the equivalent expressions by means of Gram determinants amount to assuming, for the operator D in the equation of motion, instead of (1c) or the equivalent (21),

$$D = [\sqrt{\rho} \ln \rho]_{\perp \mathcal{L}\{\sqrt{\rho}R_i\}} + \sum_j \alpha_j [\sqrt{\rho}R_j]_{\perp \mathcal{L}\{\sqrt{\rho} \ln \rho, \sqrt{\rho}R_{i \neq j}\}}, \quad (\text{E.1})$$

where the explicit expression for the j -th term in the summation is obtained from the ratio of determinants in (21c) by interchanging everywhere $\sqrt{\rho} \ln \rho$ with $\sqrt{\rho}R_j$ so that

$$\alpha_j = \tau(\rho) \dot{r}_j \frac{\Gamma(\sqrt{\rho} \ln \rho, \{\sqrt{\rho}R_{i \neq j}\})}{\Gamma(\sqrt{\rho} \ln \rho, \{\sqrt{\rho}R_i\})}. \quad (\text{E.2})$$

Geometrically, the additional terms are in the steepest- r_j -ascent direction compatible with maintaining constant the mean values of the other generators and the entropy.

Analogous obvious extension to the composite system case can be obtained by assuming for the operator D_J , instead of (2c),

$$D_J = [\sqrt{\rho_J}(B \ln \rho)^J]_{\perp \mathcal{L}\{\sqrt{\rho_J}(R_i)^J\}} + \sum_j \alpha_j^J [\sqrt{\rho_J}(R_j)^J]_{\perp \mathcal{L}\{\sqrt{\rho_J}(B \ln \rho)^J, \sqrt{\rho_J}(R_{i \neq j})^J\}}, \quad (\text{E.3})$$

with the α_j^J 's such that

$$\dot{r}_j = \sum_{J=1}^M \frac{\alpha_j^J}{\tau_J(\rho)} \frac{\Gamma(\sqrt{\rho_J}(B \ln \rho)^J, \{\sqrt{\rho_J}(R_i)^J\})}{\Gamma(\sqrt{\rho_J}(B \ln \rho)^J, \{\sqrt{\rho_J}(R_{i \neq j})^J\})}. \quad (\text{E.4})$$

Appendix F. Extension to other entropy or mean value functionals

For the purposes of quantum thermodynamics, in our view the necessary entropy functional is $-k_B \text{Tr}(\rho \ln \rho)$, for the reasons given in [7, 9, 11, 13, 16, 18, 24].

However, in view of the recent literature on nonextensive quantum theories, as suggested also in [3], it may be useful to note that the entire formalism of our equation of motion can be readily reformulated in the case of any other well-behaved entropy functional $s(\rho)$ and set of nonlinear generator functionals $r_i(\rho)$.

For the single constituent system it suffices to substitute throughout the operator $(-2k_B \sqrt{\rho} I) + 2\sqrt{\rho} S = (-2k_B \sqrt{\rho}) - 2k_B \sqrt{\rho} \ln \rho$ (notice that in the Gram determinants the addenda in parantheses cancel out) with the new entropy gradient operator, $\partial s(\rho)/\partial \sqrt{\rho}$, and the operators $2\sqrt{\rho} R_i$ with [operators which when symmetrized ($\{A, A^\dagger\}/2$) are equal to] the gradient operators of the new generator functionals, $\partial r_i(\rho)/\partial \sqrt{\rho}$.

However, for a composite system, consistently with the nonextensivity of these theories, it may be difficult or not at all possible to identify the operators corresponding to $(S)^J$ and $(R_i)^J$ representing the subsystems' local perceptions of the entropy and the generators.

Appendix G. A noteworthy equation for a composite system that fails to meet a separability condition

It is interesting to note that the role of the $\sqrt{\rho_J}$ operators in (2) [and that of $\sqrt{\rho}$ in (1)] is formally useful but only auxiliary, because wherever there is a $\sqrt{\rho_J}$, another $\sqrt{\rho_J}$ comes in front or behind it. In fact, in [10] the equation of motion was in terms of ρ_J only. We realized the usefulness of the $\sqrt{\rho_J}$ formalism only later, in connection with the proof of the steepest-entropy-ascent geometric property [13].

By allowing a more relevant role of the $\sqrt{\rho}$ operator [30], an alternative to the construction in (108) might appear formally better, and suggest the apparently alternative equation of motion based on the following definitions

$$E_D = - \sum_{J=1}^M \frac{1}{2\tau_J(\rho)} D'_J \otimes \sqrt{\rho_J}, \quad (\text{G.1})$$

$$(\sqrt{\rho} F)_{\check{J}}^J = \text{Tr}_{\bar{J}}[(I_J \otimes \sqrt{\rho_{\bar{J}}}) \sqrt{\rho} F], \quad (\text{G.2})$$

$$D'_J = [(\sqrt{\rho} \ln \rho)_{\check{J}}^J]_{\perp \mathcal{L}\{(\sqrt{\rho})_{\check{J}}^J, (\sqrt{\rho} H)_{\check{J}}^J, [(\sqrt{\rho} G_i)_{\check{J}}^J]\}}. \quad (\text{G.3})$$

In fact, it can be readily verified that for a given F on \mathcal{H} with $[F, H] = 0$ the rate of change of $\text{Tr}(\rho F)$ would be zero if and only if $(\sqrt{\rho} F)_{\check{J}}^J$ is in $\mathcal{L}\{(\sqrt{\rho})_{\check{J}}^J, (\sqrt{\rho} H)_{\check{J}}^J, [(\sqrt{\rho} G_i)_{\check{J}}^J]\}$, and so $\text{Tr}(\rho)$, $\text{Tr}(\rho H)$, and $\text{Tr}(\rho G_i)$ would be conserved. The expressions for the rate of entropy generation, the Onsager relations and the other results would be almost identical to those obtained from our equation, except for the substitution throughout of $\sqrt{\rho_J}(F)^J$ with $(\sqrt{\rho} F)_{\check{J}}^J$.

However, the resulting dynamics would fail to satisfy at least the important property expressed by (78), because it can be verified that if $H = H_J \otimes I_{\bar{J}} + I_J \otimes H_{\bar{J}}$ but $\rho \neq \rho_J \otimes \rho_{\bar{J}}$ then separate conservation of the non-interacting subsystem's energy would not be guaranteed.

References

- [1] Domokos G and Kovesi-Domokos S 1999 *J. Phys. A* **32** 4105
- [2] Czachor M 1998 *Phys. Rev. A* **57** 4122; Czachor M and Kuna M 1998 *Phys. Rev. A* **58** 128; Czachor M and Naudts J 1999 *Phys. Rev. E* **59** R2497
- [3] Gheorghiu-Svirschevski S 2001 *Phys. Rev. A* **63** 022105 and the Addendum, Gheorghiu-Svirschevski S 2001 *Phys. Rev. A* **63** 054102
- [4] For an account of the vast literature on these applications see the following papers and references therein: Weinberg S 1989 *Phys. Rev. Lett.* **62** 485; Stern A, Aharonov Y and Imry Y 1990 *Phys. Rev. A* **41** 3436; Ekert A K 1991 *Phys. Rev. Lett.* **67** 661; Holyst J A and Turski L A 1992 *Phys. Rev. A* **45** 6180; Vidal G and Werner R F 1993 *Phys. Rev. A* **65** 032314; Unruh W G and Wald R M 1995 *Phys. Rev. D* **52** 2176; Bennett C H et al 1996 *Phys. Rev. Lett.* **76** 722; Grigorescu M 1998 *Physica A* **256** 149; Miranowicz A, Matsueda H and Wahiddin M R B 2000 *J. Phys. A* **33** 5159
- [5] Englman R 2002 appendix in Lemanska M and Jaeger Z 2002 *Physica D* **170** 72
- [6] Aerts D et al 2003 *Phys. Rev. E* **67** 051926
- [7] Hatsopoulos G N and Gyftopoulos E P 1976 *Found. Phys.* **6** 15; Hatsopoulos G N and Gyftopoulos E P 1976 *Found. Phys.* **6** 127; Hatsopoulos G N and Gyftopoulos E P 1976 *Found. Phys.* **6** 439; Hatsopoulos G N and Gyftopoulos E P 1976 *Found. Phys.* **6** 561
- [8] We use the term “revolutionary” in the sense introduced by Kuhn T S 1970 *The Structure of Scientific Revolutions* (Chicago: The University of Chicago Press)
- [9] Gyftopoulos E P and Çubukçu E 1997 *Phys. Rev. E* **55** 3851
- [10] Beretta G P 1981 *On the General Equation of Motion of Quantum Thermodynamics and the Distinction between Quantal and Nonquantal Uncertainties* (Cambridge, MA: Massachusetts Institute of Technology Sc.D. thesis, unpublished); Beretta G P 2005 *arXiv:quant-ph* 0509116
- [11] Beretta G P, Gyftopoulos E P, Park J L and Hatsopoulos G N 1984 *Nuovo Cimento B* **82** 169; Beretta G P, Gyftopoulos E P and Park J L 1985 *Nuovo Cimento B* **87** 77
- [12] Beretta G P 2009 *Rep. Math. Phys.* **64** 139
- [13] Beretta G P 1986 *Frontiers of Nonequilibrium Statistical Physics (NATO Advanced Study Institute Series B: Physics vol 135) (Proc. June 1984 NATO ASI Conf. Santa Fe, NM, June 1984)* ed G T Moore and M O Scully (New York: Plenum Press) p 193 and p 205; Beretta G P 1986 *The Physics of Phase Space (Lecture Notes in Physics vol 278)* ed Y S Kim and W W Zachary (New York: Springer-Verlag) p 441
- [14] Beretta G P 1985 *Int. J. Theor. Phys.* **24** 119
- [15] Beretta G P 1985 *Int. J. Theor. Phys.* **24** 1233
- [16] Beretta G P 1987 *Found. Phys.* **17** 365
- [17] Beretta G P 1986 *Computer-Aided Engineering of Energy Systems (ASME Book H0341C)* ed R A Gaggioli (New York: ASME) p 129; Beretta G P 1987 *Second Law Analysis of Thermal Systems (ASME Book I00236)* ed M J Moran and E Sciubba (New York: ASME) p 17; Beretta G P 1987 *Second Law Analysis of Heat Transfer in Energy Systems (ASME Book G00390 HTD vol 80)* ed R F Boehm and N Lior (New York: ASME) p 31
- [18] For interpretative discussions see also: Beretta G P 1987 *Proc. ANAE-ONERA-CERT Int. Symp. on Stability (Paris)* (Toulouse: Centre d'Etudes et de Recherches), p 87; Beretta G P 1992 *Proc. 1991 Taormina Conf. on Thermodynamics*, edited by P V Giaquinta, M Vicentini Missoni and F Wanderlingh (Messina: Atti dell'Accademia Peloritana dei Pericolanti vol LXX-1) p 61
- [19] Maddox J 1985 *Nature* **316** 11
- [20] Korsch H J and Steffen H 1987 *J. Phys. A* **20** 3787; Hensel M and Korsch H J 1992 *J. Phys. A* **25** 2043
- [21] Janussis A 1985 *Lett. Nuovo Cimento* **43** 309
- [22] Onsager L 1931 *Phys. Rev.* **37** 405; Onsager L 1931 *Phys. Rev.* **38** 2265; Casimir H B G 1945 *Rev. Mod. Phys.* **17** 34; Kubo R 1957 *J. Phys. Soc. Jpn.* **12** 570
- [23] Callen H B 1947 (Cambridge, MA: Massachusetts Institute of Technology Sc.D. thesis, unpublished); Callen H B, Barasch M L and Jackson J L 1952 *Phys. Rev.* **88** 1382; Callen H B and Welton T A 1951 *Phys. Rev.* **83** 34; Greene R F and Callen H B 1951 *Phys. Rev.* **83** 1231; Greene R F and Callen H B 1952 *Phys. Rev.* **88** 1387; Callen H B and Greene R F 1952 *Phys. Rev.* **86** 702; Onsager L and Machlup S 1953 *Phys. Rev.* **91** 1505.
- [24] Gyftopoulos E P 2001 *J. Energy Resources Technology (ASME Transactions)* **123** 110
- [25] Ellis J, Lopez J L, Mavromatos N E and Nanopoulos D V 1996 *Phys. Rev. D* **53** 3846 and references therein.
- [26] See, e.g., Gallis M R 1991 *Phys. Rev. A* **45** 47; Reznik B 1996 *Phys. Rev. Lett.* **76** 1192; Grigorescu M 1998 *Physica A* **256** 149 and references therein.
- [27] See, e.g., Kostin M D 1972 *J. Chem. Phys.* **57** 3589; Bialinicki-Birula I and Mycielski J 1976 *Ann. Phys. (N.Y.)* **100** 62; Hasse R W 1975 *J. Math. Phys.* **16** 2005; Gisin N 1981 *J. Phys. A: Math. Gen.* **14** 2259; Schuch D, Chung K-M and Hartmann H 1983 *J. Math. Phys.* **24** 1652; van Wonderen A J and Lendi K 2000 *J. Phys. A* **33** 5757; Tuszyński J A and Dixon J M 2001 *Physica A* **290** 69
- [28] Öttinger H C 2001 *Phys. Rev. E* **62** 4720
- [29] Equation (21d) is obtained from (21c) by subtracting from each row (except the second) the second row multiplied by second element of that row. As a result, the second column entries become all zero except the second which is unity, and so it can be eliminated together with the second row.
- [30] The $\rho = \gamma\gamma^\dagger$ formalism proposed by Reznik [26] and adopted by Gheorghiu-Svirschevski [3], extends

our $\rho = (\sqrt{\rho})^2$ formalism but, as shown in the present paper, is not necessary to derive our equation. Conceptually, it is troublesome because it leaves unspecified the choice of γ for a given ρ , and risks to imply the existence of yet unidentified physical observables that would render the state operator insufficient. Formally, it may suggest the adoption of (G.1-G.3) for a composite system (properly extended to the complex square root formalism), which has many correct properties but fails to meet a necessary separability requirement (see Appendix G).

- [31] See references [1] in [3].
- [32] Beretta G P 1986 *J. Math. Phys.* **27** 305. The technical conjecture proposed therein was later found proved in Hiai F, Ohya M and Tsukada M 1981 *Pacific J. Math.* **96** 99
- [33] This equivalence is well known and must be traced to Hatsopoulos G N and Keenan J H 1965 *Principles of General Thermodynamics* (New York: Wiley). It has been further clarified in Keenan J H, Hatsopoulos G N and Gyftopoulos E P 1972 *Principles of Thermodynamics* (Chicago: Encyclopaedia Britannica) and fully developed in Gyftopoulos E P and Beretta G P 2005 *Thermodynamics: Foundations and Applications* (Mineola: Dover) (first edition 1991 New York: Macmillan)
- [34] See, e.g., Margenau H 1936 *Phys. Rev.* **49** 240; Margenau H 1963 *Philosophy of Science* **30** 6; Park J L 1968 *Philosophy of Science* **35** 3; Park J L 1968 *Am. J. Phys.* **36** 211; Gyftopoulos E P and von Spakovsky M R 2007 *Proc. ECOS07: Keynotes* (Padova: ASME) p 69
- [35] This notation includes the special cases in which subsystem J consists of only, say, the 4-th type of particle (in which case N_{iJ} is the null operator for every $i \neq 4$) possibly with a fixed amount, say, 5 particles (in which case $N_{4J} = 5I_J$). Note that some N_{iJ} may be the null operator if subsystem J does not contain particles of type i . Even in this case the set of generators $\{R_{iJ}\}$ remains well-defined.
- [36] By *strictly isolated* we mean that the system interacts with no other systems and at some time (and, hence, at all times) is in an independent state when viewed as a subsystem of any conceivable composite system containing it.
- [37] As shown in [11], $\text{Tr}(\rho \dot{B} \ln \rho) = 0$ by the definition of B .
- [38] For rigorous proofs, the reader is referred to the original papers, where only some technical general aspects of the mathematics of the nonlinear equation for $\dim \mathcal{H} = \infty$ were left unresolved or based on technical conjectures, especially those related to the global stability of the thermodynamic equilibrium states, the instability or metastability of the other equilibrium states and all boundary solutions and limit cycles, and the existence and uniqueness in the general case of all solutions both forward and backwards in time, i.e., for $-\infty < t < \infty$. For a two-level system, instead, all these proofs are complete [14]. The work in [3] provides a further proof of preservation of positivity. That in [32] completes the proofs regarding stability.
- [39] See, e.g., Messiah A 1976 *Quantum Mechanics* (New York: Wiley) p 320