

Positive Nonlinear Dynamical Group Uniting Quantum Mechanics and Thermodynamics

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Abstract

We discuss and motivate the form of the generator of a nonlinear quantum dynamical group “designed” so as to accomplish a unification of quantum mechanics (QM) and thermodynamics. We call this nonrelativistic theory Quantum Thermodynamics (QT). Its conceptual foundations differ from those of (von Neumann) quantum statistical mechanics (QSM) and (Jaynes) quantum information theory (QIT), but for thermodynamic equilibrium (TE) states it reduces to the same mathematics, and for zero entropy states it reduces to standard unitary QM. By restricting the discussion to a strictly isolated system (non-interacting, disentangled and uncorrelated) we show how the theory departs from the conventional QSM/QIT rationalization of the second law of thermodynamics. The nonlinear dynamical group of QT is construed so that the second law emerges as a theorem of existence and uniqueness of a stable equilibrium state for each set of mean values of the energy and the number of constituents. To achieve this QT assumes $-k_B \text{Tr} \rho \ln \rho$ for the physical entropy and is designed to implement two fundamental ansatzs. The first is that in addition to the standard QM states described by idempotent density operators (zero entropy), a strictly isolated system admits also states that must be described by non-idempotent density operators (nonzero entropy). The second is that for such additional states the law of causal evolution is determined by the simultaneous action of a Schrödinger-von Neumann-type Hamiltonian generator and a nonlinear dissipative generator which conserves the mean values of the energy and the number of constituents, and (in forward time) drives the density operator in the ‘direction’ of steepest entropy ascent (maximal entropy increase). The resulting positive nonlinear dynamical group (not just a semi-group) is well-defined for all nonequilibrium states, no matter how far from TE. Existence and uniqueness of solutions of the (Cauchy) initial state problem for all density operators, implies that the equation of motion can be solved not only in forward time, to describe relaxation towards TE, but also backwards in time, to reconstruct the ‘ancestral’ or primordial lowest entropy state or limit cycle from which the system originates.

1 Introduction

Several authors have attempted to construct a microscopic theory that includes a formulation of the second law of thermodynamics [1, 2, 3, 4, 5, 6, 7, 8]. Some

approaches strive to derive irreversibility from a change of representation of reversible unitary evolution, others from a change from the von Neumann entropy functional to other functionals, or from the loss of information in the transition from a deterministic system to a probabilistic process, or from the effect of coupling with one or more heat baths.

We discuss the key elements and features of a different non-standard theory which introduces *de facto* an ansatz of “intrinsic entropy and intrinsic irreversibility” at the fundamental level [9, 10], and an additional ansatz of “steepest entropy ascent” which entails an explicit well-behaved dynamical principle and the second law of thermodynamics. To present it, we first discuss an essential fundamental concept.

2 States of a strictly isolated individual system

Let us consider a system A and denote by R the rest of the universe, so that the Hilbert space of the universe is $\mathcal{H}_{AR} = \mathcal{H}_A \otimes \mathcal{H}_R$. We restrict our attention to a “strictly isolated” system A , by which we mean that at all times, $-\infty < t < \infty$, A is uncorrelated (and hence disentangled) from R , i.e., $\rho_{AR} = \rho_A \otimes \rho_R$, and non-interacting, i.e., $H_{AR} = H_A \otimes I_R + I_A \otimes H_R$.

Many would object at this point that with this premise the following discussion should be dismissed as useless and unnecessary, because no “real” system is ever strictly isolated. We reject this argument as counterproductive, misleading and irrelevant, for we recall that Physics is a conceptual edifice by which we attempt to model and unify our perceptions of the empirical world (physical reality [11]). Abstract concepts such as that of a strictly isolated system and that of a state of an individual system not only are well-defined and conceivable, but have been keystones of scientific thinking, indispensable for example to structure the principle of causality. In what other framework could we introduce, say, the time-dependent Schrödinger equation?

Because the dominant theme of quantum theory is the necessity to accept that the notion of state involves probabilistic concepts in an essential way [12], established practices of experimental science impose that the construct “probability” be linked to the relative frequency in an “ensemble”. Thus, the purpose of a quantum theory is to regularize purely probabilistic information about the measurement results from a “real ensemble” of identically prepared identical systems. An important scheme for the classification of ensembles, especially emphasized by von Neumann [13], hinges upon the concept of ensemble “homogeneity”. Given an ensemble it is always possible to conceive of it as subdivided into many sub-ensembles. An ensemble is homogeneous iff every conceivable subdivision results into sub-ensembles all identical to the original (two sub-ensembles are identical iff upon measurement on both of the same physical observable at the same time instant, the outcomes yield the same arithmetic mean, and this holds for all conceivable physical observables). It follows that each individual member system of a homogeneous ensemble has exactly the same intrinsic characteristics as any other member, which therefore define the “state” of the individual system. In other words, the empirical correspondent of the abstract concept of “state of an individual system” is the homogeneous ensemble (sometimes also called “pure” [14, 15, 16] or “proper” [17, 18]).

We restrict our attention to the states of a strictly isolated individual system.

By this we rule out from our present discussion all heterogeneous preparations, such as those considered in QSM and QIT, which are obtained by statistical composition of different homogeneous component preparations. Therefore, we concentrate on the intrinsic characteristics of each individual system and their irreducible, non-statistical probabilistic nature.

3 Broader quantum kinematics ansatz

According to standard QM the states of a strictly isolated individual system are in one-to-one correspondence with the one-dimensional orthogonal projection operators on the Hilbert space of the system. We denote such projectors by the symbol P . If $|\psi\rangle$ is an eigenvector of P such that $P|\psi\rangle = |\psi\rangle$ and $\langle\psi|\psi\rangle = 1$ then $P = |\psi\rangle\langle\psi|$. It is well known that differently from classical states, quantum states are characterized by irreducible intrinsic probabilities. We need not elaborate further on this point. We only recall that $-\text{Tr}P \ln P = 0$.

Instead, we adhere to the ansatz [19] that the set of states in which a strictly isolated individual system may be found is broader than conceived in QM, specifically that it is in one-to-one correspondence with the set of linear operators ρ on \mathcal{H} , with $\rho^\dagger = \rho$, $\rho > 0$, $\text{Tr}\rho = 1$, without the restriction $\rho^2 = \rho$. We call these the “state operators” to emphasize that they play the same role that in QM is played by the projectors P , and that they are associated with the homogeneous preparation schemes. This fundamental ansatz has been first proposed by Hatsopoulos and Gyftopoulos [19]. It allows an implementation of the second law of thermodynamics at the fundamental level in which the physical entropy, given by $s(\rho) = -k_B \text{Tr}\rho \ln \rho$, emerges as an intrinsic microscopic and non-statistical property of matter, in the same sense as the (mean) energy $e(\rho) = \text{Tr}\rho H$ is an intrinsic property.

We first assume that our isolated system is an indivisible constituent of matter, i.e., one of the following:

- A single strictly isolated d -level particle, in which case $\mathcal{H} = \mathcal{H}_d = \bigoplus_{k=0}^d \mathcal{H}_{e_k}$ where e_k is the k -th eigenvalue of the (one-particle) Hamiltonian H_1 and \mathcal{H}_{e_k} the corresponding eigenspace). Even if the system is isolated, we do not rule out fluctuations in energy measurement results and hence we do not assume a “microcanonical” Hamiltonian (i.e., $H = e_{\tilde{k}} P_{\mathcal{H}_{e_{\tilde{k}}}}$ for some \tilde{k}) but we assume a full “canonical” Hamiltonian $H = H_1 = \sum_k e_k P_{\mathcal{H}_{e_k}}$.
- A strictly isolated ideal Boltzmann gas of non-interacting identical indistinguishable d -level particles, in which case \mathcal{H} is a Fock space, $\mathcal{H} = \mathcal{F}_d = \bigoplus_{n=0}^{\infty} \mathcal{H}_d^{\otimes n}$. Again, we do not rule out fluctuations in energy nor in the number of particles, and hence we do not assume a canonical number operator (i.e., $N = \tilde{z} P_{\mathcal{H}_d^{\otimes \tilde{z}}}$ for some \tilde{z}) but we assume a full grand canonical number operator $N = \sum_{n=0}^{\infty} n P_{\mathcal{H}_d^{\otimes n}}$ and a full Hamiltonian $H = \sum_{n=0}^{\infty} H_n P_{\mathcal{H}_d^{\otimes n}}$ where $H_n = \sum_{J=1}^n (H_1)_J \otimes I_{\overline{J}}$ is the n -particle Hamiltonian on $\mathcal{H}_d^{\otimes n}$, $(H_1)_J$ denotes the one-particle Hamiltonian on the J -th particle space $(\mathcal{H}_d)_J$ and $I_{\overline{J}}$ the identity operator on the direct product space $\bigotimes_{K=1, K \neq J}^n (\mathcal{H}_d)_K$ of all other particles. Note that $[H, N] = 0$.
- A strictly isolated ideal Fermi-Dirac or Bose-Einstein gas of non-interacting

identical indistinguishable d -level particles, in which case \mathcal{H} is the anti-symmetric or symmetric subspace, respectively, of the Boltzmann Fock space just defined.

We further fix ideas by considering the simplest quantum system, a 2-level particle, a qubit. It is well known [20] that using the 3-vector $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ of Pauli spin operators, $[\sigma_j, \sigma_k] = \epsilon_{jkl}\sigma_l$, we can represent the Hamiltonian operator as $H = \hbar\omega(\frac{1}{2}I + \mathbf{h} \cdot \boldsymbol{\sigma})$ where \mathbf{h} is a unit-norm 3-vector of real scalars (h_1, h_2, h_3) , and the density operators as $\rho = \frac{1}{2}I + \mathbf{r} \cdot \boldsymbol{\sigma}$ where \mathbf{r} is a 3-vector of real scalars (r_1, r_2, r_3) with norm $r = |\mathbf{r}| \leq 1$, and $r = 1$ iff ρ is idempotent, $\rho^2 = \rho$.

If the 2-level particle is strictly isolated, its states in standard QM are one-to-one with the unit-norm vectors ψ in \mathcal{H} or, equivalently, the unit-trace one-dimensional projection operators on \mathcal{H} , $P_\psi = |\psi\rangle\langle\psi|$, i.e., the idempotent density operators $\rho^2 = \rho$. Hence, in the 3-dimensional euclidean space (r_1, r_2, r_3) , states map one-to-one with points on the unit radius 2-dimensional spherical surface, $r = 1$, the ‘‘Bloch sphere’’. The mean value of the energy is $e(\rho) = \text{Tr}\rho H = \frac{1}{2}(1 + \mathbf{h} \cdot \mathbf{r})$ and is clearly bounded by $0 \leq e(\rho) \leq \hbar\omega$. The set of states that share a given mean value of the energy are represented by the 1-dimensional circular intersection between the Bloch sphere and the constant mean energy plane orthogonal to \mathbf{h} defined by the $\mathbf{h} \cdot \mathbf{r} = \text{const}$ condition. The time evolution according to the Schrödinger equation $\dot{\psi} = -iH\psi/\hbar$ or, equivalently, $\dot{P}_\psi = -i[H, P_\psi]/\hbar$ or [20] $\dot{\mathbf{r}} = \omega\mathbf{h} \times \mathbf{r}$ yields a periodic precession of \mathbf{r} around \mathbf{h} along such 1-dimensional circular path on the surface of the Bloch sphere. At the end of every (Poincaré) cycle the strictly isolated system passes again through its initial state: a clear pictorial manifestation of the reversibility of Hamiltonian dynamics.

At the level of a strictly isolated qubit, the Hatsopoulos-Gyftopoulos ansatz amounts to accepting that the two-level system admits also states that must be described by points inside the Bloch sphere, not just on its surface, even if the qubit is noninteracting and uncorrelated. The eigenvalues of ρ are $(1 \pm r)/2$, therefore the isoentropic surfaces are concentric spheres,

$$s(\rho) = s(r) = -k_B \left(\frac{1+r}{2} \ln \frac{1+r}{2} + \frac{1-r}{2} \ln \frac{1-r}{2} \right). \quad (1)$$

The highest entropy state with given mean energy is at the center of the disk obtained by intersecting the Bloch sphere with the corresponding constant energy plane. Such states all lie on the diameter along the direction of the Hamiltonian vector \mathbf{h} and are thermodynamic equilibrium (maximum entropy principle [21]).

Next, we construct our extension of the Schrödinger equation of motion valid inside the Bloch sphere. By assuming such law of causal evolution, the second law will emerge as a theorem of the dynamics.

4 Steepest-entropy-ascent ansatz

Let us return to the general formalism for a strictly isolated system. We go back to the qubit example at the end of the section.

As a first step to force positivity and hermiticity of the state operator ρ we

assume an equation of motion of the form

$$\frac{d\rho}{dt} = \rho E(\rho) + E^\dagger(\rho) \rho = \sqrt{\rho} \left(\sqrt{\rho} E(\rho) \right) + \left(\sqrt{\rho} E(\rho) \right)^\dagger \sqrt{\rho} , \quad (2)$$

where $E(\rho)$ is a (non-hermitian) operator-valued (nonlinear) function of ρ that we call the “evolution” operator. Without loss of generality, we write $E = E_+ + iE_-$ where $E_+ = (E + E^\dagger)/2$ and $E_- = (E - E^\dagger)/2i$ are hermitian operators, so that Eq. (2) takes the form

$$\frac{d\rho}{dt} = -i[E_-(\rho), \rho] + \{E_+(\rho), \rho\} , \quad (3)$$

with $[\cdot, \cdot]$ and $\{\cdot, \cdot\}$ the usual commutator and anti-commutator, respectively.

We consider the space of linear (not necessarily hermitian) operators on \mathcal{H} equipped with the real scalar product

$$(F|G) = \text{Tr}(F^\dagger G + G^\dagger F)/2 , \quad (4)$$

so that for any time-independent hermitian observable R on \mathcal{H} , the rate of change of the mean value $r(\rho) = \text{Tr}(\rho R) = (\sqrt{\rho}|\sqrt{\rho}R)$ can be written as

$$\frac{dr(\rho)}{dt} = \text{Tr}\left(\frac{d\rho}{dt} R\right) = 2 (\sqrt{\rho}E|\sqrt{\rho}R) , \quad (5)$$

from which it follows that a set of $r_i(\rho)$'s is time invariant iff $\sqrt{\rho}E$ is orthogonal to the linear span of the set of operators $\sqrt{\rho}R_i$, that we denote by $\mathcal{L}\{\sqrt{\rho}R_i\}$.

For an isolated system, we therefore require that, for every ρ , operator $\sqrt{\rho}E$ be orthogonal [in the sense of scalar product (4)] to the linear manifold $\mathcal{L}\{\sqrt{\rho}R_i\}$ where the set $\{\sqrt{\rho}R_i\}$ always includes $\sqrt{\rho}I$, to preserve $\text{Tr}\rho = 1$, and $\sqrt{\rho}H$, to conserve the mean energy $e(\rho) = \text{Tr}\rho H$. For a field of indistinguishable particles we also include $\sqrt{\rho}N$ to conserve the mean number of particles $n(\rho) = \text{Tr}\rho N$. For a free particle we would include $\sqrt{\rho}P_x, \sqrt{\rho}P_y, \sqrt{\rho}P_z$ to conserve the mean momentum vector $\mathbf{p}(\rho) = \text{Tr}\rho\mathbf{P}$, but here we omit this case for simplicity [30].

Similarly, the rate of change of the entropy functional can be written as

$$\frac{ds(\rho)}{dt} = (\sqrt{\rho}E | -2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho]) , \quad (6)$$

where the operator $-2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho]$ may be interpreted as the gradient (in the sense of the functional derivative) of the entropy functional $s(\rho) = -k_B \text{Tr}\rho \ln \rho$ with respect to operator $\sqrt{\rho}$ (for the reasons why in our theory the physical entropy is represented by the von Neumann functional, see Refs. [19, 22]).

It is noteworthy that the Hamiltonian evolution operator

$$E_H = iH/\hbar , \quad (7)$$

is such that $\sqrt{\rho}E_H$ is orthogonal to $\mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H, \sqrt{\rho}N\}$ as well as to the entropy gradient operator $-2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho]$. It yields a Schrödinger-Liouville-von Neumann unitary dynamics

$$\frac{d\rho}{dt} = \rho E_H + E_H^\dagger \rho = -\frac{i}{\hbar} [H, \rho] , \quad (8)$$

which maintains time-invariant all the eigenvalues of ρ . Because of this feature, all time-invariant (equilibrium) density operators according to Eq. (8) (those that commute with H) are globally stable [23] with respect to perturbations that do not alter the mean energy (and the mean number of particles). As a result, for given values of the mean energy $e(\rho)$ and the mean number of particles $n(\rho)$ such a dynamics would in general imply many stable equilibrium states, contrary to the second law requirement that there must be only one (this is the well-known Hatsopoulos-Keenan statement of the second law [24], which entails [21] the other well-known statements by Clausius, Kelvin, and Carathéodory).

Therefore, we assume that in addition to the Hamiltonian term E_H , the evolution operator E has an additional component E_D ,

$$E = E_H + E_D , \quad (9)$$

that we will take so that $\sqrt{\rho}E_D$ is at any ρ orthogonal both to $\sqrt{\rho}E_H$ and to the intersection of the linear manifold $\mathcal{L}\{\sqrt{\rho}R_i\}$ with the isoentropic hypersurface to which ρ belongs (for a two level system, such intersection is a one-dimensional planar circle inside the Bloch sphere). In other words, we assume that $\sqrt{\rho}E_D$ is proportional to the component of the entropy gradient operator $-2k_B [\sqrt{\rho} + \sqrt{\rho} \ln \rho]$ orthogonal to $\mathcal{L}\{\sqrt{\rho}R_i\}$,

$$\sqrt{\rho}E_D = -\frac{1}{2\tau(\rho)} [\sqrt{\rho} \ln \rho]_{\perp \mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H(\cdot, \sqrt{\rho}N)\}} , \quad (10)$$

where we denote the “constant” of proportionality by $1/2\tau(\rho)$ and use the fact that $\sqrt{\rho}$ has no component orthogonal to $\mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H(\cdot, \sqrt{\rho}N)\}$.

It is important to note that the “intrinsic dissipation” or “intrinsic relaxation” characteristic time $\tau(\rho)$ is left unspecified in our construction and need not be a constant. All our results hold as well if $\tau(\rho)$ is some reasonably well behaved positive definite functional of ρ . The empirical and/or theoretical determination of $\tau(\rho)$ is a most challenging open problem in our research program. For example, it has been suggested [25] that the experiments by Franzen [26] (intended to evaluate the spin relaxation time constant of vapor under vanishing pressure conditions) and by Kukolich [27] (intended to provide a laboratory validation of the time-dependent Schrödinger equation) both suggest some evidence of an intrinsic relaxation time.

Using standard geometrical notions, we can show [9, 10, 28, 29] that given any set of linearly independent operators $\{\sqrt{\rho}R_i\}$ spanning $\mathcal{L}\{\sqrt{\rho}I, \sqrt{\rho}H(\cdot, \sqrt{\rho}N)\}$ the dissipative evolution operator takes the explicit expression

$$\sqrt{\rho}E_D = \frac{1}{2k_B\tau(\rho)} \sqrt{\rho}\Delta M(\rho) \quad (11)$$

where $M(\rho)$ is a “Massieu-function” operator defined by

$$M(\rho) = \frac{\begin{vmatrix} S & R_1 & \cdots & R_i & \cdots \\ \langle \Delta S \Delta R_1 \rangle & \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_i \Delta R_1 \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta S \Delta R_i \rangle & \langle \Delta R_1 \Delta R_i \rangle & \cdots & \langle \Delta R_i \Delta R_i \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\Gamma(\{\sqrt{\rho}R_i\})} , \quad (12)$$

and we use the notation (F and G hermitian)

$$S = -k_B P_{\text{Ran } \rho} \ln \rho, \quad (13)$$

$$\Delta F = F - \text{Tr}(\rho F)I, \quad (14)$$

$$\langle \Delta F \Delta G \rangle = (\sqrt{\rho} \Delta F | \sqrt{\rho} \Delta G) = \frac{1}{2} \text{Tr}(\rho \{ \Delta F, \Delta G \}), \quad (15)$$

$$\Gamma(\{ \sqrt{\rho} R_i \}) = \det[\langle \Delta R_i \Delta R_j \rangle] \quad (\text{a Gram determinant}). \quad (16)$$

The Massieu-function operator defined by Eq. (12) generalizes to any non-equilibrium state the well-known equilibrium Massieu characteristic function $s(\rho_{TE}) - \beta e(\rho_{TE}) + \beta \mu n(\rho_{TE})$. As a result, our full equation of motion takes the form

$$\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] + \frac{1}{2k_B \tau(\rho)} \{ \Delta M(\rho), \rho \}. \quad (17)$$

Gheorghiu-Svirschewski [30] re-derived our nonlinear equation of motion from a variational principle that in our notation may be cast as follows [29],

$$\max_{\sqrt{\rho} E_D} \frac{ds(\rho)}{dt} \quad \text{subject to} \quad \frac{dr_i(\rho)}{dt} = 0 \quad \text{and} \quad (\sqrt{\rho} E_D | \sqrt{\rho} E_D) = c^2(\rho), \quad (18)$$

where $r_0(\rho) = \text{Tr} \rho$, $r_1(\rho) = \text{Tr} H \rho$, $r_2(\rho) = \text{Tr} N \rho$, and $c^2(\rho)$ is some positive functional. The last constraint means that we are not really searching for “maximal entropy production” but only for the direction of steepest entropy ascent, leaving unspecified the rate at which such direction “attracts” the state of the system. The necessary condition in terms of Lagrange multipliers is

$$\frac{\partial}{\partial \sqrt{\rho} E_D} \frac{ds}{dt} - \sum_i \lambda_i \frac{\partial}{\partial \sqrt{\rho} E_D} \frac{dr_i}{dt} - \lambda_0 \frac{\partial}{\partial \sqrt{\rho} E_D} (\sqrt{\rho} E_D | \sqrt{\rho} E_D) = 0, \quad (19)$$

and, using Eqs. (5) and (6) becomes

$$-2k_B(\sqrt{\rho} + \sqrt{\rho} \ln \rho) - 2 \sum \lambda_i \sqrt{\rho} R_i - 2\lambda_0 \sqrt{\rho} E_D = 0, \quad (20)$$

which inserted in the constraints and solved for the multipliers yields Eq. (11).

The resulting rate of entropy change (entropy generation by irreversibility, for the system is isolated) is given by the equivalent expressions

$$\frac{ds(\rho)}{dt} = -k_B \frac{d \text{Tr} \rho \ln \rho}{dt} = 4k_B \tau(\rho) (\sqrt{\rho} E_D | \sqrt{\rho} E_D) \quad (21)$$

$$= \frac{k_B}{\tau(\rho)} \frac{\Gamma(\sqrt{\rho} \ln \rho, \{ \sqrt{\rho} R_i \})}{\Gamma(\{ \sqrt{\rho} R_i \})} = \frac{1}{k_B \tau(\rho)} \frac{\Gamma(\sqrt{\rho} S, \{ \sqrt{\rho} R_i \})}{\Gamma(\{ \sqrt{\rho} R_i \})} \geq 0. \quad (22)$$

Because a Gram determinant $\Gamma(\sqrt{\rho} X_1, \dots, \sqrt{\rho} X_N) = \det[\langle \Delta X_i \Delta X_j \rangle]$ is either strictly positive or zero iff operators $\{ \sqrt{\rho} X_i \}$ are linearly dependent, the rate of entropy generation is either a positive semi-definite nonlinear functional of ρ , or it is zero iff operators $\sqrt{\rho} S, \sqrt{\rho} I, \sqrt{\rho} H, \sqrt{\rho} N$ are linearly dependent, i.e., iff the state operator is of the form

$$\rho = \frac{B \exp[-\beta H (+\nu N)] B}{\text{Tr}(B \exp[-\beta H (+\nu N)])}, \quad (23)$$

for some “binary” projection operator B ($B^2 = B$, eigenvalues either 0 or 1) and some real scalar(s) β (and ν). Non-dissipative states are therefore all and only the density operators that have the nonzero eigenvalues “canonically” (or “grand canonically”) distributed. For them, $\sqrt{\rho}E_D = 0$ and our equation of motion (17) reduces to the Schrödinger–von Neumann form $i\hbar\dot{\rho} = [H, \rho]$. Such states are either equilibrium states, if $[B, H] = 0$, or belong to a limit cycle and undergo a unitary hamiltonian dynamics, if $[B, H] \neq 0$, in which case

$$\rho(t) = B(t) \exp[-\beta H (+\nu N)] B(t) / \text{Tr}[B(t) \exp[-\beta H (+\nu N)]] , \quad (24)$$

$$B(t) = U(t) B(0) U^{-1}(t) , \quad U(t) = \exp(-itH/\hbar) . \quad (25)$$

For $\text{Tr}B = 1$ the states (23) reduce to the (zero entropy) states of standard QM, and obey the standard unitary dynamics generated by the usual time-dependent Schrödinger equation. For $B = I$ we have the maximal-entropy (thermodynamic-equilibrium) states, which turn out to be the only globally stable equilibrium states of our dynamics, so that the Hatsopoulos-Keenan statement of the second law emerges as an exact and general dynamical theorem.

Indeed, in the framework of our extended theory, all equilibrium states and limit cycles that have at least one null eigenvalue of ρ are unstable. This is because any neighboring state operator with one of the null eigenvalues perturbed (i.e., slightly “populated”) to a small value ϵ (while some other eigenvalues are slightly changed so as to ensure that the perturbation preserves the mean energy and the mean number of constituents), would eventually proceed “far away” towards a new partially-maximal-entropy state or limit cycle with a canonical distribution which fully involves also the newly “populated” eigenvalue while the other null eigenvalues remain zero.

It is clear that the canonical (grand-canonical) density operators $\rho_{TE} = \exp[-\beta H (+\nu N)] / \text{Tr}(\exp[-\beta H (+\nu N)])$ are the only stable equilibrium states, i.e., the TE states of the strictly isolated system. They are mathematically identical to the density operators which also in QSM and QIT are associated with TE, on the basis of their maximizing the von Neumann indicator of statistical uncertainty $-\text{Tr}\rho \ln \rho$ subject to given values of $\text{Tr}H\rho$ (and $\text{Tr}N\rho$). Because maximal entropy mathematics in QSM and QIT successfully represents TE physical reality, our theory, by entailing the same mathematics for the stable equilibrium states, preserves all the successful results of equilibrium QSM and QIT. However, within QT such mathematics takes up an entirely different physical meaning. Indeed, each density operator here does not represent statistics of measurement results from a “heterogeneous” ensemble, as in QSM and QIT where, according to von Neumann’s recipe [13, 31], the “intrinsic” uncertainties (irreducibly introduced by standard QM) are mixed with the “extrinsic” uncertainties (related to the heterogeneity of its preparation, i.e., to not knowing the exact state of each individual system in the ensemble). In QT, instead, each density operator, including the maximal-entropy stable TE ones, represents “intrinsic” uncertainties only, because it is associated with a homogeneous preparation and, therefore, it represents the state of each and every individual system of the homogeneous ensemble.

We noted elsewhere [33] that the fact that our nonlinear equation of motion preserves the null eigenvalues of ρ , i.e., conserves the cardinality $\dim \text{Ker}(\rho)$ of the set of zero eigenvalues, is an important physical feature consistent with recent experimental tests (see the discussion of this point in Ref. [30] and ref-

erences therein) that rule out, for pure (zero entropy) states, deviations from linear and unitary dynamics and confirm that initially unoccupied eigenstates cannot spontaneously become occupied. This fact, however, adds nontrivial experimental and conceptual difficulties to the problem of designing fundamental tests capable, for example, of ascertaining whether decoherence originates from uncontrolled interactions with the environment due to the practical impossibility of obtaining strict isolation, or else it is a more fundamental intrinsic feature of microscopic dynamics requiring an extension of QM like the one we propose.

For a confined, strictly isolated d -level system, our equation of motion for non-zero entropy states ($\rho^2 \neq \rho$) takes the following forms [20, 34]. If the Hamiltonian is fully degenerate [$H = eI$, $e(\rho) = e$ for every ρ],

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\tau}(\rho \ln \rho - \rho \text{Tr} \rho \ln \rho) , \quad (26)$$

while if the Hamiltonian is nondegenerate,

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\tau} \frac{\begin{vmatrix} \rho \ln \rho & \rho & \frac{1}{2}\{H, \rho\} \\ \text{Tr} \rho \ln \rho & 1 & \text{Tr} \rho H \\ \text{Tr} \rho H \ln \rho & \text{Tr} \rho H & \text{Tr} \rho H^2 \end{vmatrix}}{\text{Tr} \rho H^2 - (\text{Tr} \rho H)^2} . \quad (27)$$

In particular, for a non-degenerate two-level system, it may be expressed in terms of the Bloch sphere representation (for $0 < r < 1$) as [20]

$$\dot{\mathbf{r}} = \omega \mathbf{h} \times \mathbf{r} - \frac{1}{\tau} \left(\frac{1-r^2}{2r} \ln \frac{1-r}{1+r} \right) \frac{\mathbf{h} \times \mathbf{r} \times \mathbf{h}}{1 - (\mathbf{h} \cdot \mathbf{r})^2} \quad (28)$$

from which it is clear that the dissipative term lies in the constant mean energy plane and is directed towards the axis of the Bloch sphere identified by the Hamiltonian vector \mathbf{h} . The nonlinearity of the equation does not allow a general explicit solution, but on the central constant-energy plane, i.e., for initial states with $\mathbf{r} \cdot \mathbf{h} = 0$, the equation implies [20]

$$\frac{d}{dt} \ln \frac{1-r}{1+r} = -\frac{1}{\tau} \ln \frac{1-r}{1+r} \quad (29)$$

which, if τ is constant, has the solution

$$r(t) = \tanh \left[-\exp \left(-\frac{t}{\tau} \right) \ln \frac{1-r(0)}{1+r(0)} \right] . \quad (30)$$

This, superposed with the precession around the hamiltonian vector, results in a spiraling approach to the maximal entropy state (with entropy $k_B \ln 2$). Notice, that the spiraling trajectory is well-defined and within the Bloch sphere for all times $-\infty < t < +\infty$, and if we follow it backwards in time it approaches as $t \rightarrow -\infty$ the limit cycle which represents the standard QM (zero entropy) states evolving according to the Schrödinger equation.

This example shows quite explicitly a general feature of our nonlinear equation of motion which follows from the existence and uniqueness of its solutions for any initial density operator both in forward and backward time. This feature

is a consequence of two facts: (1) that zero eigenvalues of ρ remain zero and therefore no eigenvalue can cross zero and become negative, and (2) that $\text{Tr}\rho$ is preserved and therefore if initially one it remains one. Thus, the eigenvalues of ρ remain positive and less than unity. On the conceptual side, it is also clear that our theory implements a strong causality principle by which all future as well as all past states are fully determined by the present state of the isolated system, and yet the dynamics is physically (thermodynamically) irreversible. Said differently, if we formally represent the general solution of the Cauchy problem by $\rho(t) = \Lambda_t \rho(0)$ the nonlinear map Λ_t is a group, i.e., $\Lambda_{t+u} = \Lambda_t \Lambda_u$ for all t and u , positive and negative. The map is therefore “invertible”, in the sense that $\Lambda_{-t} = \Lambda_t^{-1}$, where the inverse map is defined by $\rho(0) = \Lambda_t^{-1} \rho(t)$.

It is a nontrivial observation that the non-invertibility of the dynamical map is not at all necessary to represent a physically irreversible dynamics. Yet, innumerable attempts to build irreversible theories start from the assertion that in order to represent thermodynamic irreversibility the dynamical map should be non-invertible. The arrow of time in our view is not to be sought for in the impossibility to retrace past history, but in the spontaneous tendency of any physical system to internally redistribute its energy (and, depending on the system, its other conserved properties such number of particles, momentum, angular momentum) along the path of steepest entropy ascent.

5 Onsager reciprocity

The intrinsically irreversible dynamics entailed by the dissipative (non-hamiltonian) part of our nonlinear equation of motion also entails an Onsager reciprocity theorem. To see this, we first note that any density operator ρ can be written as [36]

$$\rho = \frac{B \exp(-\sum_j f_j X_j) B}{\text{Tr} B \exp(-\sum_j f_j X_j)}, \quad (31)$$

where the possibly time-dependent Boolean B is such that $B = P_{\text{Ran}\rho} (= I - P_{\text{Ker}\rho})$ and the time-independent operators X_j together with the identity I form a set such that their restrictions to $\mathcal{H}' = B\mathcal{H}$, $\{I', X'_j\}$ span the real space of hermitian operators on $\mathcal{H}' = B\mathcal{H}$. Hence,

$$\sqrt{\rho} \ln \rho = -f_0 \sqrt{\rho} - \sum_j f_j \sqrt{\rho} X_j, \quad (32)$$

$$x_j(\rho) = \text{Tr}(\rho X_j), \quad (33)$$

$$s(\rho) = k_B f_0 + k_B \sum_j f_j x_j(\rho), \quad (34)$$

$$\text{where } k_B f_j = \left. \frac{\partial s(\rho)}{\partial x_j(\rho)} \right|_{x_{i \neq j}(\rho)} \quad (35)$$

may be interpreted as a “generalized affinity” or force. Defining

$$\frac{Dx_i(\rho)}{Dt} = 2 (E_D | \sqrt{\rho} X_i). \quad (36)$$

as “the dissipative rate of change” of the mean value $x_j(\rho)$, we find

$$\frac{Dx_i(\rho)}{Dt} = \sum_j f_j L_{ij}(\rho), \quad (37)$$

where the coefficients $L_{ij}(\rho)$ (nonlinear in ρ) may be interpreted as “generalized conductivities” and are given explicitly (no matter how far ρ is from TE) by

$$\begin{aligned}
L_{ij}(\rho) &= L_{ji}(\rho) = \frac{1}{\tau(\rho)} \left([\sqrt{\rho}X_i]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}} \mid [\sqrt{\rho}X_j]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}} \right) \quad (38) \\
&= \frac{1}{\tau(\rho)} \frac{\begin{vmatrix} \langle \Delta X_i \Delta X_j \rangle & \langle \Delta R_1 \Delta X_j \rangle & \cdots & \langle \Delta R_k \Delta X_j \rangle & \cdots \\ \langle \Delta X_i \Delta R_1 \rangle & \langle \Delta R_1 \Delta R_1 \rangle & \cdots & \langle \Delta R_k \Delta R_1 \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle \Delta X_i \Delta R_k \rangle & \langle \Delta R_1 \Delta R_k \rangle & \cdots & \langle \Delta R_k \Delta R_k \rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\Gamma(\{\sqrt{\rho}R_k\})}, \quad (39)
\end{aligned}$$

and therefore form a symmetric, non-negative definite Gram matrix $[L_{ij}(\rho)]$, which is strictly positive iff all operators $[\sqrt{\rho}X_i]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}}$ are linearly independent.

The rate of entropy generation may be rewritten as a quadratic form of the generalized affinities,

$$\frac{ds(\rho)}{dt} = k_B \sum_i \sum_j f_i f_j L_{ij}(\rho). \quad (40)$$

If all operators $[\sqrt{\rho}X_i]_{\perp\mathcal{L}\{\sqrt{\rho}R_i\}}$ are linearly independent, $\det[L_{ij}(\rho)] \neq 0$ and Eq. (37) may be solved to yield

$$f_j = \sum_i L_{ij}^{-1}(\rho) \frac{Dx_i(\rho)}{Dt}, \quad (41)$$

and the rate of entropy generation can be written also as a quadratic form of the dissipative rates

$$\frac{ds(\rho)}{dt} = k_B \sum_i \sum_j L_{ij}^{-1}(\rho) \frac{Dx_i(\rho)}{Dt} \frac{Dx_j(\rho)}{Dt}. \quad (42)$$

6 Composite systems and reduced dynamics

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 distinguishable and indivisible elementary constituent subsystems. For example:

- A strictly isolated composite of r distinguishable d -level particles, in which case $\mathcal{H} = \otimes_{J=1}^r \mathcal{H}_{d_J}$ and $H = \sum_{J=1}^r (H_1)_J \otimes I_{\bar{J}} + V$ where V is some interaction operator over \mathcal{H} .
- A strictly isolated ideal mixture of r types of Boltzmann, Fermi-Dirac or Bose-Einstein gases of non-interacting identical indistinguishable d_J -level particles, $J = 1, \dots, r$, in which case \mathcal{H} is a composite of Fock spaces

$\mathcal{H} = \otimes_{J=1}^r \mathcal{F}_{d_J} = \oplus_{n_1=0}^{\infty} \cdots \oplus_{n_r=0}^{\infty} \mathcal{H}_{d_1}^{\otimes n_1} \otimes \cdots \otimes \mathcal{H}_{d_r}^{\otimes n_r}$ where the factor Fock spaces belonging to Fermi-Dirac (Bose-Einstein) components are restricted to their antisymmetric (symmetric) subspaces. Again, we assume full grand-canonical number operators $N_J = \sum_{n_J=0}^{\infty} n_J P_{\mathcal{H}_{d_J}^{\otimes n_J}}$ and Hamiltonian $H = \sum_{J=1}^r I_{\bar{J}} \otimes \sum_{n_J=0}^{\infty} H_{n_J} P_{\mathcal{H}_{d_J}^{\otimes n_J}} + V$.

For compactness of notation we denote the subsystem Hilbert spaces as

$$\mathcal{H} = \mathcal{H}^1 \otimes \mathcal{H}^2 \otimes \cdots \otimes \mathcal{H}^r = \mathcal{H}^J \otimes \mathcal{H}^{\bar{J}}, \quad (43)$$

where \bar{J} denotes all subsystems except the J -th one. The overall system is strictly isolated in the sense already defined, and the Hamiltonian operator

$$H = \sum_{J=1}^r H_J \otimes I_{\bar{J}} + V, \quad (44)$$

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

The subdivision into elementary constituents, considered as indivisible, and reflected by the structure of the Hilbert space \mathcal{H} as a direct product of subspaces, is particularly important because it defines the level of description of the system and specifies its elementary structure. The system's internal structure we just defined determines the form of the nonlinear dynamical law proposed by this author [28, 29, 37] to implement the steepest entropy ascent ansatz in a way compatible with the obvious self-consistency ‘‘separability’’ and ‘‘locality’’ requirements [33]. It is important to note that, because our dynamical principle is nonlinear in the density operator, we cannot expect the form of the equation of motion to be independent of the system's internal structure.

The equation of motion that we ‘‘designed’’ in [28, 37] so as to guarantee all the necessary features (that we list in Ref. [33]), is

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \sum_{J=1}^r \frac{1}{2k_B \tau_J(\rho)} \{(\Delta M_J(\rho))^J, \rho_J\} \otimes \rho_{\bar{J}}, \quad (45)$$

where we use the notation [see Ref. [29] for interpretation of $(S)^J$ and $(H)^J$]

$$\sqrt{\rho_J}(\Delta M_J(\rho))^J = \left[\sqrt{\rho_J}(S)^J \right]_{\perp \mathcal{L}\{\sqrt{\rho_J}(R_{i_J})^J\}}, \quad (46)$$

$$\mathcal{L}\{\sqrt{\rho_J}(R_{i_J})^J\} = \text{lin. span of } \sqrt{\rho_J}I_J, \sqrt{\rho_J}(H_J)^J, \sqrt{\rho_J}(N_{k_J})^J \quad (47)$$

$$(F_J|G_J)_J = \text{Tr}_J(F_J^\dagger G_J + G_J^\dagger F_J)/2, \quad (48)$$

$$(R_{i_J})^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}})R_{i_J}], \quad (49)$$

$$(S)^J = \text{Tr}_{\bar{J}}[(I_J \otimes \rho_{\bar{J}})S], \quad (50)$$

and the ‘‘internal redistribution characteristic times’’ $\tau_J(\rho)$'s are some positive constants or positive functionals of the overall system's density operator ρ .

All the results found for the single constituent extend in a natural way to the composite system. For example, the rate of entropy change becomes

$$\frac{ds(\rho)}{dt} = \sum_{J=1}^r \frac{1}{k_B \tau_J(\rho)} \frac{\Gamma(\sqrt{\rho_J}(S)^J, \{\sqrt{\rho_J}(R_{i_J})^J\})}{\Gamma(\{\sqrt{\rho_J}(R_{i_J})^J\})}. \quad (51)$$

The dynamics reduces to the Schrödinger-von Neumann unitary Hamiltonian dynamics when, for each J , there are multipliers λ_{iJ} such that

$$\sqrt{\rho_J}(S)^J = \sqrt{\rho_J} \sum_i \lambda_{iJ} (R_{iJ})^J. \quad (52)$$

The equivalent variational formulation is

$$\max_{\{\sqrt{\rho_J} E_{D,J}\}} \frac{ds(\rho)}{dt} \text{ subject to } \frac{dr_i(\rho)}{dt} = 0 \text{ and } (\sqrt{\rho_J} E_{D,J} | \sqrt{\rho_J} E_{D,J})_J = c_J^2(\rho), \quad (53)$$

where $r_0(\rho) = \text{Tr}\rho$, $r_1(\rho) = \text{Tr}H\rho$, $r_2(\rho) = \text{Tr}N\rho$, and $c_J^2(\rho)$ are some positive functionals of ρ . The last constraints, one for each subsystem, mean that each subsystem contributes to the overall evolution (for the dissipative non-hamiltonian part) by pointing towards its “local perception” of the direction of steepest (overall) entropy ascent, each with an unspecified intensity (which depends on the values of the functionals $c_J(\rho)$, that are inversely related to the internal redistribution characteristic times $\tau_J(\rho)$).

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

$$\frac{d\rho_A}{dt} = -\frac{i}{\hbar}[H_A, \rho_A] + \frac{1}{k_B} \sum_{\substack{J=1 \\ J \in A}}^r \frac{1}{2\tau_J(\rho)} \{(\Delta M_J(\rho))^J, \rho_J\} \otimes (\rho_A)_{\overline{J}}, \quad (54)$$

$$\frac{d\rho_B}{dt} = -\frac{i}{\hbar}[H_B, \rho_B] + \frac{1}{k_B} \sum_{\substack{J=1 \\ J \in B}}^r \frac{1}{2\tau_J(\rho)} \{(\Delta M_J(\rho))^J, \rho_J\} \otimes (\rho_B)_{\overline{J}}, \quad (55)$$

where $(\rho_A)_{\overline{J}} = \text{Tr}_J(\rho_A)$, $(\rho_B)_{\overline{J}} = \text{Tr}_J(\rho_B)$, and operators $(\Delta M_J(\rho))^J$ result independent of H_B for every $J \in A$ and independent of H_A for every $J \in B$. Therefore, all functionals of ρ_A (local observables) remain unaffected by whatever change in B , i.e., locality problems are excluded.

7 Concluding remarks

According to QSM and QIT, the uncertainties that are measured by the physical entropy, are to be regarded as either extrinsic features of the heterogeneity of an ensemble or as witnesses of correlations with other systems. Instead, we discuss an alternative theory, QT, based on the Hatsopoulos-Gyftopoulos fundamental ansatz [19, 31] that also such uncertainties are irreducible (and hence, “physically real” and “objective” like standard QM uncertainties) in that they belong to the state of the individual system, even if uncorrelated and even if a member of a homogeneous ensemble.

According to QT, second law limitations emerge as manifestations of such additional physical and irreducible uncertainties. The Hatsopoulos-Gyftopoulos ansatz not only makes a unified theory of QM and Thermodynamics possible, but gives also a framework for a resolution of the century old “irreversibility paradox”, as well as of the conceptual paradox [31] about the QSM/QIT interpretation of density operators, which has preoccupied scientists and philosophers

since when Schrödinger surfaced it in Ref. [32]. This fundamental ansatz seems to respond to Schrödinger prescient conclusion in Ref. [32]: "...in a domain which the present theory (Quantum Mechanics) does not cover, there is room for new assumptions without necessarily contradicting the theory in that region where it is backed by experiment."

QT has been described as "an adventurous scheme" [38], and indeed it requires quite a few conceptual and interpretational jumps, but (1) it does not contradict any of the mathematics of either standard QM or TE QSM/QIT, which are both contained as extreme cases of the unified theory, and (2) for nonequilibrium states, no matter how "far" from TE, it offers the structured, nonlinear equation of motion proposed by this author which models, deterministically, irreversibility, relaxation and decoherence, and is based on the additional ansatz of steepest-entropy-ascent microscopic dynamics.

Many authors, in a variety of contexts [35], have observed in recent years that irreversible natural phenomena at all levels of description seem to obey a principle of general and unifying validity. It has been named [35] "maximum entropy production principle", but we note in this paper that, at least at the quantum level, the weaker concept of "attraction towards the direction of steepest entropy ascent" [9, 10, 28] is sufficient to capture precisely the essence of the second law.

We finally emphasize that the steepest-entropy-ascent, nonlinear law of motion we propose, and the dynamical group it generates (not just a semi-group), is a potentially powerful modeling tool that should find immediate application also outside of QT, namely, regardless of the dispute about the validity of the Hatsopoulos-Gyftopoulos ansatz on which QT hinges. Indeed, in view of its well-defined and well-behaved general mathematical features and solutions, our equation of motion may be used in phenomenological kinetic and dynamical theories where there is a need to guarantee full compatibility with the principle of entropy non-decrease and the second-law requirement of existence and uniqueness of stable equilibrium states (for each set of values of the mean energy, of boundary-condition parameters, and of the mean amount of constituents).

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