What is Quantum Thermodynamics?

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What is the physical significance of entropy? What is the physical origin of irreversibility? Do entropy and irreversibility exist only for complex and macroscopic systems?

For everyday laboratory physics, the *mathematical formalism* of Statistical Mechanics (canonical and grand-canonical, Boltzmann, Bose-Einstein and Fermi-Dirac distributions) allows a successful description of the thermodynamic equilibrium properties of matter, including entropy values. However, as already recognized by Schrödinger in 1936, Statistical Mechanics is impaired by *conceptual ambiguities and logical inconsistencies*, both in its explanation of the meaning of entropy and in its implications on the concept of state of a system.

An alternative theory has been developed by Gyftopoulos, Hatsopoulos and the present author to eliminate these stumbling conceptual blocks while maintaining the mathematical formalism of ordinary quantum theory, so successful in applications. To resolve both the problem of the meaning of entropy and that of the origin of irreversibility, we have built entropy and irreversibility into the laws of microscopic physics. The result is a theory that has all the necessary features to combine Mechanics and Thermodynamics uniting all the successful results of both theories, eliminating the logical inconsistencies of Statistical Mechanics and the paradoxes on irreversibility, and providing an entirely new perspective on the microscopic origin of irreversibility, nonlinearity (therefore including chaotic behavior) and maximal-entropy-generation non-equilibrium dynamics.

In this long introductory paper we discuss the background and formalism of Quantum Thermodynamics including its nonlinear equation of motion and the main general results regarding the nonequilibrium irreversible dynamics it entails. Our objective is to 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, the nonrelativistic theory that we call Quantum Thermodynamics (QT). Its conceptual foundations differ from those of (von Neumann) quantum statistical mechanics (QSM) and (Jaynes) quantum information theory (QIT), but for thermody-
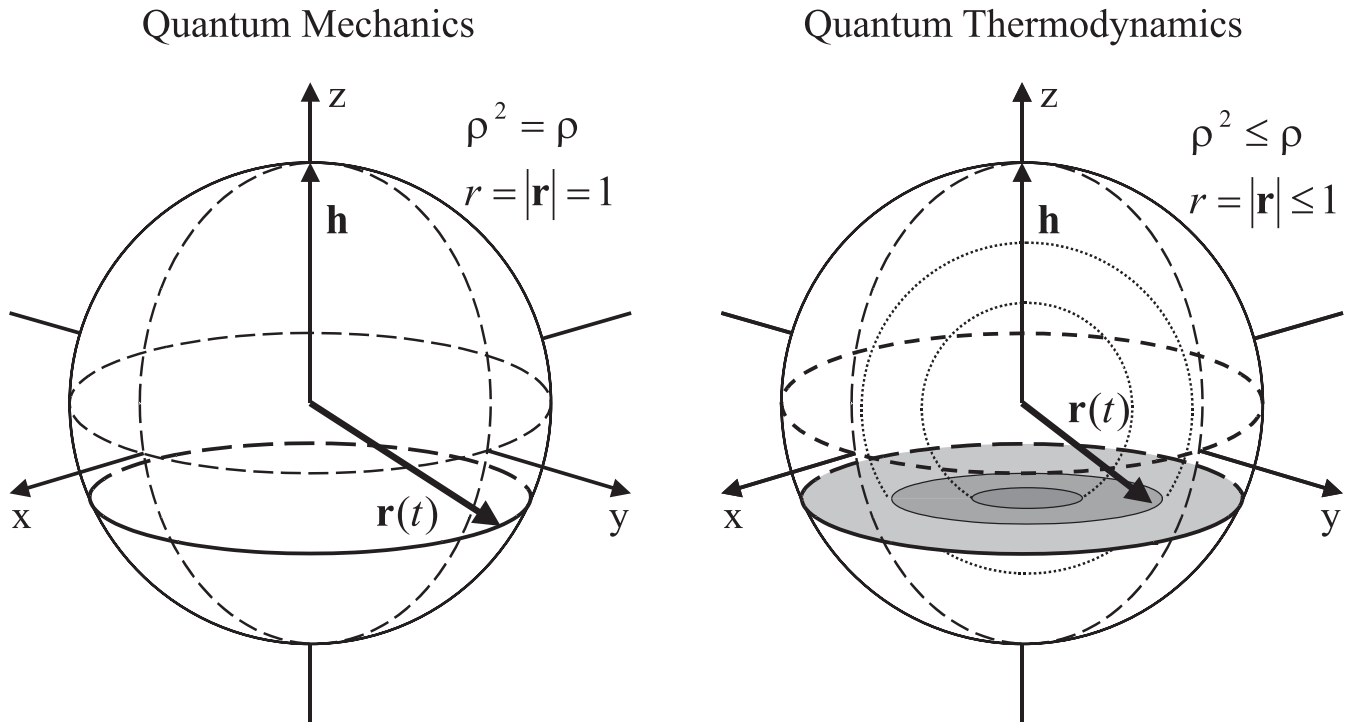
Quantum Mechanics   Quantum Thermodynamics

FIG. 1: Pictorial representation for a two level system of the augmented state domain implied by the Hatsopoulos-Gyftopoulos kinematics with respect to the state domain of standard Quantum Mechanics. For a strictly isolated and uncorrelated two level system, quantum mechanical states are in one-to-one correspondence with the surface of the Bloch sphere, $r = 1$; quantum thermodynamical states are in one-to-one correspondence with the entire sphere, surface and interior, $r \leq 1$.

namic 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 $-k_{\mathrm{B}}\mathrm{Tr}\rho\ln\rho$ 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 Schroedinger-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.

I. INTRODUCTION

There is no dispute about the results, the mathematical formalism, and the practical consequences of the theories of Mechanics and Equilibrium Thermodynamics, even though their presentations and derivations still differ essentially from author to author in logical structure and emphasis. Both Mechanics (Classical and Quantum) and Equilibrium Thermodynamics have been developed independently of one another for different applications, and have enjoyed innumerable great successes. There are no doubts that the results of these theories will remain as milestones of the development of Science.

But as soon as they are confronted, Mechanics and Equilibrium Thermodynamics give rise to an apparent incompatibility of results: a dilemma, a paradox that has concerned generations of scientists during the last century and still remains unresolved. The problem arises when the general features of kinematics and dynamics in Mechanics are confronted with the general features of kinematics and dynamics implied by Equilibrium Thermodynamics. These features are in striking conflict in the two theories. The conflict concerns the notions of reversibility, availability of energy to adiabatic extraction, and existence of stable equilibrium states [1, 2]. Though perhaps presented with emphasis on other related conflicting aspects, the apparent incompatibility of the theories of Mechanics and Equilibrium Thermodynamics is universally recognized by all scientists that have tackled the problem [3]. What is not universally recognized is how to rationalize the unconfortable paradoxical situation [1].

The rationalization attempt better accepted within the physical community is offered by the theory of Statistical Mechanics. Like several other minor attempts of rationalization [1], Statistical Mechanics stems from the premise that Mechanics and Equilibrium Thermodynamics occupy different levels in the hierarchy of physical theories: they both describe the same physical reality, but Mechanics (Quantum) is concerned with the true fundamental description, whereas Equilibrium Thermodynamics copes with the phenomenological description – in terms of a limited set of state variables – of systems with so many degrees of freedom that the fundamental quantum mechanical description would be overwhelmingly complicated and hardly reproducible.

When scrutinized in depth, this almost universally accepted premise and, therefore, the conceptual foundations of Statistical Mechanics are found to be shaky and unsound. For example, they seem to require that we abandon the concept of state of a system [4], a keystone of traditional physical thought. In spite of the lack of a sound conceptual framework, the mathematical formalism and the results of Statistical Mechanics have enjoyed such great successes that the power of its methods have deeply convinced almost the entire physical community that the conceptual problems can be safely ignored.

The formalism of Statistical Mechanics has also provided mathematical tools to attempt the extension of the results beyond the realm of thermodynamic equilibrium. In this area, the results have been successful in a variety of specific nonequilibrium problems. The many attempts to synthetize and generalize the results have generated important conclusions such as the Boltzmann equation, the Onsager reciprocity relations, the fluctuation- dissipation relations, and the Master equations. But, again, the weakness of the conceptual foundations has forbidden so far the development of a sound unified theory of nonequilibrium.

The situation can be summarized as follows. On the one hand, the successes of Mechanics, Equilibrium Thermodynamics, and the formalism of Statistical Mechanics for both equilibrium and nonequilibrium leave no doubts

on the validity of their end results. On the other hand, the need remains of a coherent physical theory capable of encompassing these same results within a sound unified unambiguous conceptual framework.

Of course, the vast majority of physicists would argue that there is no such need because there is no experimental observation that Statistical Mechanics cannot rationalize. But the problem at hand is not that there is a body of experimental evidence that cannot be regularized by current theories. Rather, it is that current theories have been developed and can be used only as ad-hoc working tools, successful to regularize the experimental evidence, but incapable to resolve conclusively the century-old fundamental questions on the physical roots of entropy and irreversibility, and on the general description of nonequilibrium. These fundamental questions have kept the scientific community in a state of tension for longer than a century and cannot be safely ignored.

In short, the irreversibility paradox, the dilemma on the meaning of entropy, and the questions on the nature of nonequilibrium phenomena remain by and large unresolved problems. The resolution of each of these problems requires consideration of all of them at once, because they are all intimately interrelated.

The notion of stability of equilibrium has played and will play a central role in the efforts to fill the gap. Of the two main schools of thought that during the past few decades have attacked the problem, the Brussels school has emphasized the role of instability and bifurcations in self-organization of chemical and biological systems, and the Keenan school at MIT has emphasized that the essence of the second law of Thermodynamics is a statement of existence and uniqueness of the stable equilibrium states of a system.

The recognition of the central role that stability plays in Thermodynamics [5] is perhaps one of the most fundamental discoveries of the physics of the last four decades, for it has provided the key to a coherent resolution of the entropy-irreversibility-nonequilibrium dilemma. In this article: first, we review the conceptual and mathematical framework of the problem; then, we discuss the role played by stability in guiding towards a coherent resolution; and, finally, we discuss the resolution offered by the new theory – Quantum Thermodynamics – proposed by the Keenan school at MIT about twenty years ago (and, short of a definitive experimental proof or disproof, still only marginally recognized by the orthodox physical community [6]).

Even though Quantum Thermodynamics is based on conceptual premises that are indeed quite revolutionary and entirely different from those of Statistical Mechanics, we emphasize the following:

- In terms of *mathematical formalism*, Quantum Thermodynamics differs from Statistical Mechanics mainly in the equation of motion which is nonlinear, even though it reduces to the Schrödinger equation for all the states of Quantum Mechanics, i.e., all zero-entropy states.

- In terms of *physical meaning*, instead, the differences are drastic. The significance of the *state operator* of Quantum Thermodynamics is entirely different from that of the *density operator* of Statistical Mechanics, even though the two are mathematically equivalent, and not only because they obey different equations of motion. Quantum Thermodynamics postulates that the set of true quantum states of a system is much broader than the set contemplated in Quantum Mechanics.

- Conceptually, the augmented set of true quantum states is a revolutionary postulate with respect to traditional quantum physics, although from the point of view of statistical mechanics practitioners, the new theory is not as traumatic as it seems.

- Paradoxically, the engineering thermodynamics community has already implicitly accepted the fact that entropy, exactly like energy, is a true physical property of matter and, therefore, the range of 'true states' of a system is much broader than that of Mechanics (zero entropy), for it must include the whole set of nonzero-entropy states.

- The new theory retains the whole mathematical formalism of Statistical Mechanics as regards thermodynamic (stable) equilibrium states – the formalism used by physics practitioners every day – but reinterprets it within a unified conceptual and mathematical structure in an entirely new way which resolves the open conceptual questions on the nature of quantum states and on irreversibility paradox, and by proposing the steepest-entropy-ascent dynamical principle opens new vistas on the fundamental description of non-equilibrium states, offering a powerful general equation for irreversible dynamics valid no matter how far from thermodynamic equilibrium.

II. THE COMMON BASIC CONCEPTUAL FRAMEWORK OF MECHANICS AND THERMODYNAMICS

In this section, we establish the basic conceptual framework in which both Mechanics and Equilibrium Thermodynamics are embedded. To this end, we define the basic terms that are traditional keystones of the kinematic and dynamic description in all physical theories, and are essential in the discussion that follows. Specifically, we review the

concepts of constituent, system, property, state, equation of motion, process, reversibility, equilibrium, and stability of equilibrium [7].

The idea of a constituent of matter denotes a specific molecule, atom, ion, elementary particle, or field, that for a given description is considered as indivisible. Within a given level of description, the constituents are the elementary building blocks. Clearly, a specific molecule may be a constituent for the description of a certain class of phenomena, but not for other phenomena in which its internal structure may not be ignored and, therefore, a different level of description must be chosen.

The kind of physical laws we are concerned with here are the most fundamental, i.e., those equally applicable at every level of description, such as the great conservation principles of Mechanics.

A. Kinematics

A *system* is a (separable) collection of constituents defined by the following specifications: (a) the type and the range of values of the *amount* of each constituent; (b) the type and the range of values of each of the *parameters* which fully characterize the *external* forces exerted on the constituents by bodies other than the constituents, for example, the parameters that describe the geometrical shape of a container; and (c) the *internal* forces between constituents such as the forces between molecules, the forces that promote or inhibit a chemical reaction, the partitions that separate constituents in one region of space from constituents in another region, or the interconnections between separated parts. Everything that is not included in the system is called the *environment* or the surroundings of the system.

At any instant in time, the values of the amounts of each type of constituent and the parameters of each external force do not suffice to characterize completely the condition of the system at that time. We need, in addition, the values of all the properties at the same instant in time. A *property* is an attribute that can be evaluated by means of a set of measurements and operations which are performed on the system with reference to one instant in time and result in a value – the *value of the property* – independent of the measuring devices, of other systems in the environment, and of other instants in time. For example, the instantaneous position of a particular constituent is a property.

Some properties in a given set are *independent* if the value of each such property can be varied without affecting the value of any other property in the set. Other properties are not independent. For example, speed and kinetic energy of a molecule are not independent properties.

The values of the amounts of all the constituents, the values of all the parameters, and the values of a complete set of independent properties encompass all that can be said at an instant in time about a system and about the results of any measurement or observation that may be performed on the system at that instant in time. As such, the collection of all these values constitutes a complete characterization of the system at that instant in time: the *state* of the system.

B. Dynamics

The state of a system may change with time either spontaneously due to its internal dynamics or as a result of interactions with other systems, or both. Systems that cannot induce any effects on each other's state are called *isolated*. Systems that are not isolated can influence each other in a number of different ways.

The relation that describes the evolution of the state of a system as a function of time is called the *equation of motion*.

In classical thermodynamics, the complete equation of motion is not known. For this reason, the description of a change of state is done in terms of the end states, i.e., the initial and the final states of the system, and the effects of the interactions that are active during the change of state. Each mode of interaction is characterized by means of well-specified effects, such as the net exchanges of some additive properties across the boundaries of the interacting systems. Even though the complete equation of motion is not known, we know that it must entail some important conclusions traditionally stated as the laws of thermodynamics. These laws reflect some general and important facets of the equation of motion such as the conditions that energy is conserved and entropy cannot be destroyed.

The end states and the effects of the interactions associated with a change of state of a system are said to specify a *process*. Processes may be classified on the basis of the modes of interaction they involve. For example, a process that involves no influence from other systems is called a *spontaneous process*. Again, a process that involves interactions resulting in no external effects other than the change in elevation a weight (or an equivalent mechanical effect) is called a *weight process*.

Processes may also be classified on the basis of whether it is physically possible to annul all their effects. A process is either reversible or irreversible. A process is *reversible* if there is a way to restore *both the system and its environment*

to their respective initial states, i.e., if all the effects of the process can be annulled. A process is *irreversible* if there is no way to restore both the system and its environment to their respective initial states.

C.   Types of states

Because the number of independent properties of a system is very large even for a system consisting of a single particle, and because most properties can vary over a large range of values, the number of possible states of a system is very large. To facilitate the discussion, we classify the states of a system on the basis of their time evolution, i.e., according to the way they change as a function of time. We classify states into four types: unsteady, steady, nonequilibrium, and equilibrium. We further classify equilibrium states into three types: unstable, metastable, and stable.

Unsteady is a state that changes with time as a result of influences of other systems in its environment. *Steady* is a state that does not change with time despite the influences of other systems in the environment. *Nonequilibrium* is a state that changes spontaneously as a function of time, i.e., a state that evolves as time goes on even when the system is isolated from its environment. *Equilibrium* is a state that does not change as a function of time if the system is isolated, i.e., a state that does not change spontaneously. *Unstable equilibrium* is an equilibrium state which, upon experiencing a minute and short lived influence by a system in the environment, proceeds from then on spontaneously to a sequence of entirely different states. *Metastable equilibrium* is an equilibrium state that may be changed to an entirely different state without leaving net effects in the environment of the system, but this can be done only by means of interactions which have a finite temporary effect on the state of the environment. *Stable equilibrium* is an equilibrium state that can be altered to a different state only by interactions that leave net effects in the environment of the system.

Starting either from a nonequilibrium or from an equilibrium state that is not stable, a system can be made to cause in its environment a change of state consisting solely in the raise of a weight. In contrast, if we start from a stable equilibrium state such a raise of a weight is impossible. This impossibility is one of the consequences of the first law and the second law of thermodynamics [7].

III.   THE BASIC MATHEMATICAL FRAMEWORK OF QUANTUM THEORY

The traditional structure of a physical theory is in terms of mathematical entities associated with each basic concept, and interrelations among such mathematical entities. In general, with the concept of *system* is associated a *metric space*, and with the concept of *state* an *element* of a subset of the metric space called the *state domain*. The different elements of the state domain represent all the different possible states of the system. With the concept of *property* is associated a *real functional* defined on the state domain. Different properties are represented by different real functionals, and the value of each property at a given state is given by the value of the corresponding functional evaluated at the element in the state domain representing the state. Some of the functionals representing properties of the system may depend also on the amounts of constituents of the system and the parameters characterizing the external forces.

A.   Quantum mechanics

In Quantum Mechanics, the metric space is a *Hilbert space* $\mathcal{H}$ ($\dim\mathcal{H} \leq \infty$), the states are the elements ψ of $\mathcal{H}$, the properties are the real linear functionals of the form $\langle \psi, A\psi \rangle$ where $\langle \cdot, \cdot \rangle$ is the scalar product on $\mathcal{H}$ and A some linear operator on $\mathcal{H}$. The composition of the system is embedded in the structure of the Hilbert space. Specifically,

$$\mathcal{H} = \mathcal{H}^1 \otimes \mathcal{H}^2 \otimes \cdots \otimes \mathcal{H}^M \tag{1}$$

means that the system is composed of M distinguishable subsystems which may, for example, correspond to the different constituents. If the system is composed of a type of particle with amount that varies over a range, then a functional on the Hilbert space represents the number of particles of that kind. The parameters characterizing the external forces may appear as external parameters in some property functionals. For example, the shape of a container is embedded in the position functionals as the contour outside which the functionals are identically null. The internal forces among constituents are embedded in the explicit form of the *Hamiltonian operator H* which gives rise to the energy functional $\langle \psi, H\psi \rangle$ and determines the dynamics of the system by means of the *Schrödinger equation of motion*

$$\frac{d\psi}{dt} = -\frac{i}{\hbar} H\psi \ . \tag{2}$$

Because the solution of the Schrödinger equation can be written as

$$\psi(t) = U(t)\psi(0) \ , \tag{3}$$

where $U(t)$ is the *unitary* operator

$$U(t) = \exp(-itH/\hbar) \ , \tag{4}$$

it is standard jargon to say that the dynamics in Quantum Mechanics is unitary.

B. Statistical mechanics

The formalism of Statistical Mechanics requires as metric space the space of all self-adjoint linear operators on $\mathcal{H}$, where $\mathcal{H}$ is the same Hilbert space that Quantum Mechanics associates with the system. The "states" are the elements ρ in this metric space that are nonnegative-definite and unit-trace. We use quotation marks because in Statistical Mechanics these elements ρ, called *density operators* or *statistical operators*, are interpreted as *statistical indicators*. Each density operator is associated with a statistical mixture of different "pure states" (read "true states") each of which is represented by an idempotent density operator ρ ($\rho^2 = \rho$) so that ρ is a projection operator, $\rho = P_\psi$, onto the one-dimensional linear span of some element ψ in $\mathcal{H}$ and, as such, identifies a precise (true) state of Quantum Mechanics.

The interpretation of density operators as statistical indicators associated with statistical mixtures of different quantum mechanical states, summarizes the almost universally accepted interpretation of Statistical Mechanics [8], but is fraught with conceptual inconsistencies. For example, it stems from the premise that a system is always in one (possibly unknown) state, but implies as a logical consequence that a system may be at once in two or even more states [4]. This self-inconsistency mines the very essence of a keystone of traditional physical thought: the notion of state of a system. A most vivid discussion of this point is found in Ref. [4]. For lack of better, the inconsistency is almost universally ignored, probably with the implicit motivation that "perhaps the interpretation has some fundamental faults but the formalism is undoubtedly successful" at regularizing physical phenomena. So, let us summarize a few more points of the successful mathematical formalism.

The "states", "mixed" ($\rho^2 \neq \rho$) or "pure" ($\rho^2 = \rho$), are the self-adjoint, nonnegative-definite, unit-trace linear operators on $\mathcal{H}$. The "properties" are the real functionals defined on the "state" domain, for example, the functionals of the form $\mathrm{Tr}A\rho$ where A is some linear operator on $\mathcal{H}$ and Tr denotes the trace over $\mathcal{H}$.

The density operators that are so successful in modeling the stable equilibrium states of Thermodynamics have a mathematical expression that depends on the structure of the system. For a system with no structure such as a single-particle system, the expression is

$$\rho = \frac{\exp(-\beta H)}{\mathrm{Tr}\exp(-\beta H)} \ , \tag{5}$$

where H is the Hamiltonian operator giving rise to the energy functional $\mathrm{Tr}H\rho$ and β is a positive scalar. For a system with a variable amount of a single type of particle, the expression is

$$\rho = \frac{\exp(-\beta H + \nu N)}{\mathrm{Tr}\exp(-\beta H + \nu N)} \ , \tag{6}$$

where N is the number operator giving rise to the number-of-particle functional $\mathrm{Tr}N\rho$ and ν is a scalar. For a system with n types of particles each with variable amount, the expression is

$$\rho = \frac{\exp(-\beta H + \sum_{i=1}^{n} \nu_i N_i)}{\mathrm{Tr}\exp(-\beta H + \sum_{i=1}^{n} \nu_i N_i)} \ . \tag{7}$$

If the system is composed of M distinguishable subsystems, each consisting of n types of particles with variable amounts, the structure is embedded in that of the Hilbert space (Equation 1) and in that of the Hamiltonian and the number operators,

$$H = \sum_{J=1}^{M} H(J) \otimes I(\overline{J}) + V \ , \tag{8}$$

$$N_i = \sum_{J=1}^{M} N_i(J) \otimes I(\overline{J}) , \tag{9}$$

where $H(J)$ denotes the Hamiltonian of the J-th subsystem when isolated, V denotes the interaction Hamiltonian among the M subsystems, $N_i(J)$ denotes the number-of-particles-of-i-th-type operator of the J-th subsystem, for $i = 1, 2, \ldots, n$ and $I(\overline{J})$ denotes the identity operator on the Hilbert space $\mathcal{H}^{\overline{J}}$ composed by the direct product of the Hilbert spaces of all subsystems except the J-th one, so that the Hilbert space of the overall system $\mathcal{H} = \mathcal{H}^J \otimes \mathcal{H}^{\overline{J}}$ and the identity operator $I = I(J) \otimes I(\overline{J})$.

Of course the richness of this mathematical formalism goes well beyond the brief summary just reported. The results of Equilibrium Thermodynamics are all recovered with success and much greater detail if the thermodynamic entropy is represented by the functional

$$-k_B \operatorname{Tr}\rho \ln \rho , \tag{10}$$

where k is Boltzmann's constant. The arguments that lead to this expression and its interpretation within Statistical Mechanics will not be reported because they obviously suffer the same incurable conceptual desease as the whole accepted interpretation of Statistical Mechanics. But the formalism works, and this is what counts to address our problem.

C. Unitary dynamics

The conceptual framework of Statistical Mechanics becomes even more unsound when the question of dynamics is brought in. Given that a density operator ρ represents the "state" or rather the "statistical description" at one instant in time, how does it evolve in time? Starting with the (faulty) statistical interpretation, all books invariably report the "derivation" of the quantum equivalent of the Liouville equation, i.e., the von Neumann equation

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] , \tag{11}$$

where $[H, \rho] = H\rho - \rho H$. The argument starts from the equation induced by the Schrödinger equation (Equation 2) on the projector $P_\psi = |\psi\rangle\langle\psi|$, i.e.,

$$\frac{dP_\psi}{dt} = -\frac{i}{\hbar}[H, P_\psi] . \tag{12}$$

Then, the argument follows the interpretation of ρ as a statistical superposition of one-dimensional projectors such as $\rho = \sum_i w_i P_{\psi_i}$. The projectors P_{ψ_i} represent the endogenous description of the true but unknown state of the system and the statistical weights w_i represent the exogenous input of the statistical description. Thus, if each term P_{ψ_i} of the endogenous part of the description follows Equation 12 and the exogenous part is not changed, i.e., the w_i's are time invariant, then the resulting overall descriptor ρ follows Equation 11.

Because the solutions of the von Neumann equation are just superpositions of solutions of the Schrödinger equation written in terms of the projectors, i.e.,

$$P_{\psi(t)} = |\psi(t)\rangle\langle\psi(t)| = |U(t)\psi(0)\rangle\langle U(t)\psi(0)|$$

$$= U(t)|\psi(0)\rangle\langle\psi(0)|U^\dagger(t) = U(t)P_{\psi(0)}U^{-1}(t) ,$$

we have

$$\rho(t) = U(t)\rho(0)U^{-1}(t) , \tag{13}$$

where $U^\dagger(t) = U^{-1}(t)$ is the adjoint of the unitary operator in Equation 4 which generates the endogenous quantum dynamics. It is again standard jargon to say that the dynamics of density operators is unitary.

The von Neumann equation or, equivalently, Equation 13, is a result almost universally accepted as an indispensable dogma. But we should recall that it is fraught with the same conceptual inconsistencies as the whole intepretation of Statistical Mechanics because its derivation hinges on such interpretation.

Based on the conclusion that the density operators evolve according to the von Neumann equation, the functional $-k_B \operatorname{Tr}\rho \ln \rho$ and, therefore, the "entropy" is an invariant of the endogenous dynamics.

Here the problem becomes delicate. On the one hand, the "entropy" functional $-k_B \operatorname{Tr} \rho \ln \rho$ is the key to the successful regularization of the results of Equilibrium Thermodynamics within the Statistical Mechanics formalism. Therefore, any proposal to represent the entropy by means of some other functional [9] that increases with time under unitary dynamics is not acceptable unless it is also shown what relation the new functional bears with the entropy of Equilibrium Thermodynamics. On the other hand, the empirical fact that the thermodynamic entropy can increase spontaneously as a result of an irreversible process, is confronted with the invariance of the "entropy" functional $-k_B \operatorname{Tr} \rho \ln \rho$ under unitary dynamics. This leads to the conclusion (within Statistical Mechanics) that entropy generation by irreversibility cannot be a result of the endogenous dynamics and, hence, can only result from changes in time of the exogenous statistical description. We are left with the unconfortable conclusion that entropy generation by irreversibility is only a kind of statistical illusion.

IV. TOWARDS A BETTER THEORY

For a variety of ad-hoc reasons – statistical, phenomenological, information- theoretic, quantum-theoretic, conceptual – many investigators have concluded that the von Neumann equation of motion (Equation 11) is incomplete, and a number of modification have been attempted [10]. The attempts have resulted in ad-hoc tools valid only for the description of specific problems such as, e.g., the nonequilibrium dynamics of lasers. However, because the underlying conceptual framework has invariably been that of Statistical Mechanics, none of these attempts has removed the conceptual inconsistencies. Indeed, within the framework of Statistical Mechanics a modification of the von Neumann equation could be justified only as a way to describe the exogenous dynamics of the statistical weights, but this does not remove the conceptual inconsistencies.

The Brussels school has tried a seemingly different approach [9]: that of constructing a functional for the entropy, different from $-k_B \operatorname{Tr} \rho \ln \rho$, that would be increasing in time under the unitary dynamics generated by the von Neumann equation. The way this is done is by introducing a new "state" $\tilde{\rho}$ obtained from the usual density operator ρ by means of a transformation, $\tilde{\rho} = \Lambda^{-1}(L)\rho$, where $\Lambda^{-1}\rho$ is a superoperator on the Hilbert space $\mathcal{H}$ of the system defined as a function of the Liouville superoperator $L\cdot = [H, \cdot]/\hbar$ and such that the von Neumann equation for ρ, $d\rho/dt = -iL\rho$, induces an equation of motion for $\tilde{\rho}$, $d\tilde{\rho}/dt = -i\Lambda^{-1}(L)L\Lambda(L)\tilde{\rho}$, as a result of which the new "entropy" functional $-k_B \operatorname{Tr} \tilde{\rho} \ln \tilde{\rho}$ increases with time. Formally, once the old "state" ρ is substituted with the new "state" $\tilde{\rho}$, this approach seems tantamount to an attempt to modify the von Neumann equation, capable therefore only to describe the exogenous dynamics of the statistical description but not to unify Mechanics and Equilibrium Thermodynamics any better than done by Statistical Mechanics.

However, the language used by the Brussels school in presenting this approach during the last decades has gradually adopted a new important element with growing conviction: the idea that entropy is a microscopic quantity and that irreversibility should be incorporated in the microscopic description. However, credit for this new and revolutionary idea, as well as its first adoption and coherent implementation, must be given to the pioneers of the Keenan school at MIT [11], even though the Brussels school might have reached this conclusion through an independent line of thought. This is shown by the quite different developments the idea has produced in the two schools. Within the recent discussion on quantum entaglement and separability, 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, the question of the existence of "spontaneous decoherence" at the microscopic level is emerging as a fundamental test of standard Quantum Mechanics [6].

As we will see, the implementation proposed by the Keenan school at MIT has provided for the first time an alternative to Statistical Mechanics capable of retaining all the successful aspects of its formalism within a sound conceptual framework free of inconsistencies and drastic departures from the traditional structure of a physical theory, in particular, with no need to abandon such keystones of traditional physical thought as the concept of trajectory and the principle of causality.

V. A BROADER QUANTUM KINEMATICS

In their effort to implement the idea that entropy is a microscopic nonstatistical property of matter in the same sense as energy is a microscopic nonstatistical property, Hatsopoulos and Gyftopoulos [11] concluded that the state domain of Quantum Mechanics is too small to include all the states that a physical system can assume [12]. Indeed, the entire body of results of Quantum Mechanics has been so successful in describing empirical data that it must be retained as a whole. A theory that includes also the results of Equilibrium Thermodynamics and the successful part of the formalism of Statistical Mechanics must necessarily be an augmentation of Quantum Mechanics, a theory in which Quantum Mechanics is only a subcase.

Next came the observation that all the successes of the formalism of Statistical Mechanics based on the density operators ρ are indeed independent of their statistical interpretation. In other words, all that matters is to retain the mathematical formalism, freeing it from its troublesome statistical interpretation.

The great discovery was that all this can be achieved if we admit that *physical systems have access to many more states than those described by Quantum Mechanics* and that the set of states is in one-to-one correspondence with the set of self-adjoint, nonnegative-definite, unit-trace linear operators ρ on the same Hilbert space $\mathcal{H}$ that Quantum Mechanics associates with the system (mathematically, this set coincides with the set of density operators of Statistical Mechanics). Figure 1 gives a pictorial idea of the augmentation of the state domain implied by the Hatsopoulos-Gyftopoulos kinematics. The states considered in Quantum Mechanics are only the extreme points of the set of states a system really admits.

In terms of interpretation, the conceptual inconsistencies inherent in Statistical Mechanics are removed. The *state operators* ρ are mathematically identical to the density operators of Statistical Mechanics, but now they represent true states, in exactly the same way as a state vector ψ represents a true state in Quantum Mechanics. Statistics plays no more role, and a linear decomposition of an operator ρ has no more physical meaning than a linear decomposition of a vector ψ in Quantum Mechanics or a Fourier expansion of a function. "Monsters" [4] that are at once in two different states are removed together with the exogenous statistics. The traditional concept of state of a system is saved.

Of course, one of the most revolutionary ideas introduced by Quantum Mechanics has been the existence, within the individual state of any system, of an indeterminacy resulting in irreducible dispersions of measurement results. This indeterminacy (usually expressed as the Heisenberg uncertainty principle) is embedded in the mathematical structure of Quantum Mechanics and is fully contained in the description of states by means of vectors ψ in a Hilbert space. The indeterminacy is not removed by the augmentation of the state domain to include all the state operators ρ. Rather, a second level of indeterminacy is added for states that are not mechanical, i.e., states such that $\rho^2 \neq \rho$. Entropy, represented by the functional $-k_B \operatorname{Tr}\rho \ln \rho$, can now be interpreted as a measure of the breadth of this additional indeterminacy, which is exactly as fundamental and irreducible as the Heisenberg indeterminacy.

VI.   ENTROPY AND THE SECOND LAW WITHOUT STATISTICS

The richness of the new augmented kinematics guarantees enough room for the resolution of the many questions that must be addressed in order to complete the theory and accomplish the necessary unification. Among the questions, the first is whether the second law of thermodynamics can be part of the new theory without having to resort to statistical, phenomenological or information- theoretic arguments.

The second law is a statement of existence and uniqueness of the stable equilibrium states for each set of values of the energy functional, the number-of-particle functionals and the parameters [5, 7]. Adjoining this statement to the structure of the new kinematics leads to identify explicitly the state operators that represent stable equilibrium states, and to prove that only the functional $-k_B \operatorname{Tr}\rho \ln \rho$ can represent the thermodynamic entropy [11]. Mathematically, the states of Equilibrium Thermodynamics are represented by exactly the same operators as in Statistical Mechanics (Equations 5 to 7). Thus, the theory bridges the gap between Mechanics and Equilibrium Thermodynamics.

Among all the states that a system can access, those of Mechanics are represented by the idempotent state operators and those of Equilibrium Thermodynamics by operators of the form of Equations 5 to 7 depending on the structure of the system. Thus, the state domain of Mechanics and the state domain of Equilibrium Thermodynamics are only two very small subsets of the entire state domain of the system.

The role of stability goes far beyond the very important result just cited, namely, the unification of Mechanics and Thermodynamics within a single uncontradictory structure that retains without modification all the successful mathematical results of Mechanics, Equilibrium Thermodynamics, and Statistical Mechanics. It provides further key guidance in addressing the question of dynamics.

The question is as follows. According to the new kinematics a system can access many more states than contemplated by Quantum Mechanics. The states of Quantum Mechanics ($\rho^2 = \rho$) evolve in time according to the Schrödinger equation of motion, which can be written either as Equation 2 or as Equation 12. But how do all the other states ($\rho^2 \neq \rho$) evolve in time? Such states are beyond the realm of Quantum Mechanics and, therefore, we cannot expect to derive their time evolution from that of Mechanics. We have to find a dynamical law for these states. At first glance, in view of the breadth of the set of states in the augmented kinematics, the problem might seem extremely open to a variety of different approaches. On the contrary, instead, a careful analysis shows that the problem is very much constrained by a number of restrictions imposed by the many conditions that such a general dynamical law must satisfy. Among these conditions, we will see that the most restrictive are those related to the stability of the states of Equilibrium Thermodynamics as required by the second law.

VII.   CAUSALITY AND CRITERIA FOR A GENERAL DYNAMICAL LAW

An underlying premise of our approach is that a new theory must retain as much as possible the traditional conceptual keystones of physical thought. So far we have saved the concept of state of a system. Here we intend to save the principle of causality. By this principle, future states of an isolated system should unfold deterministically from initial states along smooth unique trajectories in the state domain. Given the state at one instant in time and complete description of the interactions, the future as well as the past should always be predictable, at least in principle.

We see no reason to conclude that [13]: "the deterministic laws of physics, which were at one point the only acceptable laws, today seem like gross simplifications, nearly a caricature of evolution." The observation that [14]: "for any dynamical system we never know the exact initial conditions and therefore the trajectory" is not sufficient reason to discard the concept of trajectory. The principle of causality and the concept of trajectory can coexist very well with all the interesting observations by the Brussels school on the relation between organization and coherent structures in chemical, biological, and fluid systems, and bifurcations born of singularities and nonlinearities of the dynamical laws. A clear example is given by the dynamical laws of fluid mechanics, which are deterministic, obey the principle of causality, and yet give rise to beautifully organized and coherent vortex structures.

Coming back to the conditions that must be satisfied by a general dynamical law, we list below the most important.

Condition 1 – Causality, forward and backward in time, and compatibility with standard Quantum Mechanics

The states of Quantum Mechanics must evolve according to the Schrödinger equation of motion. Therefore, the trajectories passing through any state ρ such that $\rho^2 = \rho$ must be entirely contained in the state domain of Quantum Mechanics, i.e., the condition $\rho^2 = \rho$ must be satisfied along the entire trajectory. This also means that no trajectory can enter or leave the state domain of Quantum Mechanics. In view of the fact that the states of Quantum Mechanics are the extreme points of our augmented state domain, the trajectories of Quantum Mechanics must be boundary solutions of the dynamical law. By continuity, there must be trajectories that approach indefinitely these boundary solutions either as $t \to -\infty$ or as $t \to +\infty$. Therefore, the periodic trajectories of Quantum Mechanics should emerge as boundary limit cycles of the complete dynamics.

Condition 2 – Conservation of energy and number of particles

If the system is isolated, the value of the energy functional $\text{Tr}H\rho$ must remain invariant along every trajectory. If the isolated system consists of a variable amount of a single type of particle with a number operator N that commutes with the Hamiltonian operator H, then also the value of the number-of-particle functional $\text{Tr}N\rho$ must remain invariant along every trajectory. If the isolated system consists of n types of particles each with variable amount and each with a number operator N_i that commutes with the Hamiltonian H, then also the value of each number-of-particle functional $\text{Tr}N_i\rho$ must remain invariant along every trajectory.

Condition 3 – Separate energy conservation for noninteracting subsystems

For an isolated system composed of two 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 noninteracting, i.e., the Hamiltonian operator $H = H_A \otimes I_B + I_A \otimes H_B$, then the functionals $\text{Tr}(H_A \otimes I_B)\rho$ and $\text{Tr}(I_A \otimes H_B)\rho$ represent the energies of the two subsystems and must remain invariant along every trajectory.

Condition 4 – Conservation of independence for uncorrelated and noninteracting subsystems

Two subsystems A and B are in independent states if the state operator $\rho = \rho_A \otimes \rho_B$, where $\rho_A = \text{Tr}_B\rho$, $\rho_B = \text{Tr}_A\rho$, Tr_B denotes the partial trace over $\mathcal{H}^B$ and Tr_A the partial trace over $\mathcal{H}^A$. For noninteracting 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. This condition guarantees that when two uncorrelated systems do not interact with each other, each evolves in time independently of the other.

Condition 5 – Stability and uniqueness of the thermodynamic equilibrium states. Second law

A state operator ρ represents an equilibrium state if $d\rho/dt = 0$. For each given set of feasible values of the energy functional $\text{Tr}H\rho$ and the number-of-particle functionals $\text{Tr}N_i\rho$ (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 below). This stable equilibrium state must represent the corresponding state of Equilibrium Thermodynamics and, therefore, must be of the form given by Equations 5 to 7. All the other equilibrium states that the dynamical law may admit must not be globally stable.

Condition 6 – Entropy nondecrease. Irreversibility

The principle of nondecrease of entropy must be satisfied, i.e., the rate of change of the entropy functional $-k_B \text{Tr}\rho\ln\rho$ along every trajectory must be nonnegative.

It is clear that with all these conditions [15] the problem of finding the complete dynamical law is not at all open to much arbitrariness.

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

VIII. LYAPUNOV STABILITY AND THERMODYNAMIC STABILITY

In order to implement Condition 5 above, we need to establish the relation between the notion of stability implied by the second law of Thermodynamics [5, 11] (and reviewed in Section 2) 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*. In this Section we review the technical definitions.

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. As sketched in Figure 2, 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 neighboring 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 with $d(u(t,\rho),\rho_e) > \eta + \epsilon$ 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 $\text{Tr}H\rho$ and $\text{Tr}N_i\rho$ (as many as required by the structure of the system), and of the parameters 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.
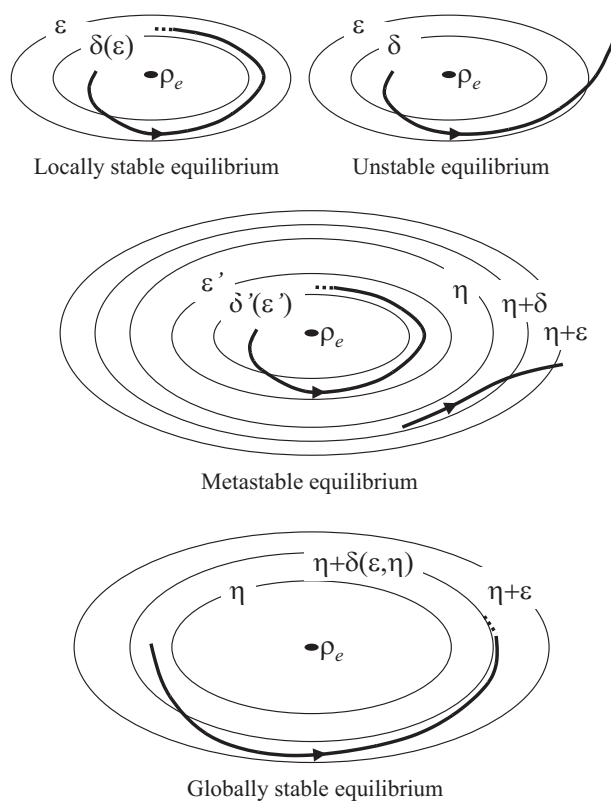
FIG. 2: Technical definitions of stability of equilibrium. Thermodynamic equilibrium states are globally stable.

For example, 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 our augmented kinematics would be expressed by an equation of motion formally identical to Equation 11 with solutions given by Equation 13 and trajectories $u(t, \rho) = U(t)\rho(0)U^{-1}(t)$ 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 $d(\rho_1, \rho_2) = \mathrm{Tr}|\rho_1 - \rho_2|$, it is easy to show [16] 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 $-k_B \mathrm{Tr}\rho \ln \rho$ plays a useful role in proving the stability of the states of Equilibrium Thermodynamics (Equations 5 to 7) provided the dynamical law guarantees that $-k_B \mathrm{Tr}u(t, \rho) \ln u(t, \rho) \geq -k_B \mathrm{Tr}\rho \ln \rho$ for every trajectory, i.e., provided Condition 6 above is satisfied. The proof of this is nontrivial and is given in Ref. [16] where, however, we also show that the entropy functional, contrary to what repeatedly emphasized by the Brussels school, is not a Lyapunov function, even if, in a strict sense [16] 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, the statement that the second law [17] "can be formulated as a dynamical principle in terms of the existence of a Lyapunov variable" would be incorrect even if the entropy were a Lyapunov variable, because it would suffice only to guarantee the 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.

IX. BUILDING ENTROPY AND IRREVERSIBILITY INTO QUANTUM THEORY

Several authors have attempted to construct a microscopic theory that includes a formulation of the second law of thermodynamics [24–31]. 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 instrinsic irreversibility" at the fundamental level [2, 32], 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.

X.   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 [33]). 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 [34], 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 [35], 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" [36–38] or "proper" [39, 40]).

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.

XI.   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 [11] 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 [11]. It allows an implementation of the second law of thermodynamics at the fundamental level in which the physical entropy, given by $s(\rho) = -k_\text{B}\text{Tr}\rho\ln\rho$, 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 $\mathcal{H} = \mathcal{H}_d = \oplus_{k=0}^d \mathcal{H}_{e_k}$ 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, $\mathcal{H} = \mathcal{F}_d = \oplus_{n=0}^\infty \mathcal{H}_d^{\otimes n}$. 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 $\otimes_{K=1, K \neq J}^n (\mathcal{H}_d)_K$ 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 antisymmetric 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 [21] that using the 3-vector $\boldsymbol{\sigma} = (\sigma_1, \sigma_2, \sigma_3)$ of Pauli spin operators, $[\sigma_j, \sigma_k] = \epsilon_{jk\ell} \sigma_\ell$, 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 $\mathcal{H}$, $P_\psi = |\psi\rangle\langle\psi|\psi\rangle^{-1}\langle\psi|$, 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 [21] $\dot{\mathbf{r}} = \omega \mathbf{h} \times \mathbf{r}$ 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 (Poincar) 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,

$$s(\rho) = s(r) = -k_{\text{B}} \left(\frac{1+r}{2} \ln \frac{1+r}{2} + \frac{1-r}{2} \ln \frac{1-r}{2} \right) . \tag{1}$$

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 [7]).

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.

XII. 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

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

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

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

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

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

$$(F|G) = \mathrm{Tr}(F^\dagger G + G^\dagger F)/2 \; , \tag{4}$$

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

$$\frac{\mathrm{d}r(\rho)}{\mathrm{d}t} = \mathrm{Tr}(\frac{\mathrm{d}\rho}{\mathrm{d}t}X) = 2\,(\sqrt{\rho}E|\,\sqrt{\rho}X) \; , \tag{5}$$

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

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 $\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})$ where the set $\sqrt{\rho}I,\{\sqrt{\rho}R_i\}$ always includes $\sqrt{\rho}I$, to preserve $\mathrm{Tr}\rho = 1$, and $\sqrt{\rho}H$, to conserve the mean energy $e(\rho) = \mathrm{Tr}\rho H$. For a field of indistinguishable particles we also include $\sqrt{\rho}N$ to conserve the mean number of particles $n(\rho) = \mathrm{Tr}\rho N$. 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 $\mathbf{p}(\rho) = \mathrm{Tr}\rho\mathbf{P}$, but here we omit this case for simplicity [47].

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

$$\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} = (\sqrt{\rho}E\,|-2k_{\mathrm{B}}\left[\sqrt{\rho} + \sqrt{\rho}\ln\rho\right]) \; , \tag{6}$$

where the operator $-2k_{\mathrm{B}}\left[\sqrt{\rho} + \sqrt{\rho}\ln\rho\right]$ may be interpreted as the gradient (in the sense of the functional derivative) of the entropy functional $s(\rho) = -k_{\mathrm{B}}\mathrm{Tr}\rho\ln\rho$ 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. [11, 41]).

It is noteworthy that the Hamiltonian evolution operator

$$E_H = iH/\hbar \; , \tag{7}$$

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 $-2k_{\mathrm{B}}\left[\sqrt{\rho} + \sqrt{\rho}\ln\rho\right]$. It yields a Schrödinger-Liouville-von Neumann unitary dynamics

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \rho\,E_H + E_H^\dagger\rho = -\frac{i}{\hbar}[H,\rho] \; , \tag{8}$$

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 [16] 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 [42], which entails [7] 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,

$$E = E_H + E_D \; , \tag{9}$$

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 $\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})$ 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 $-2k_{\mathrm{B}}\left[\sqrt{\rho} + \sqrt{\rho}\ln\rho\right]$ orthogonal to $\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})$,

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

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

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 [43] that the experiments by Franzen [44] (intended to evaluate the spin relaxation time constant of vapor under vanishing pressure conditions) and by Kukolich [45] (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 [2, 19, 32, 46] that given any set of linearly independent operators $\sqrt{\rho}I, \{\sqrt{\rho}R_i\}$ spanning $\mathcal{L}(\sqrt{\rho}I, \sqrt{\rho}H(, \sqrt{\rho}N))$ the dissipative evolution operator takes the explicit expression

$$\sqrt{\rho}E_D = \frac{1}{2k_{\mathrm{B}}\tau(\rho)}\sqrt{\rho}\Delta M(\rho) \tag{11}$$

where $M(\rho)$ is a "Massieu-function" operator defined by the following ratio of determinants

$$M(\rho) = \frac{\begin{vmatrix} S & I & \cdots & R_i & \cdots \\ & & & & \\ (\sqrt{\rho}S|\sqrt{\rho}I) & (\sqrt{\rho}I|\sqrt{\rho}I) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}I) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ (\sqrt{\rho}S|\sqrt{\rho}R_i) & (\sqrt{\rho}I|\sqrt{\rho}R_i) & \cdots & (\sqrt{\rho}R_i|\sqrt{\rho}R_i) & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\Gamma(\sqrt{\rho}I, \{\sqrt{\rho}R_i\})} , \tag{12}$$

in which we use the following notation (F, G hermitian)

$$S = -k_{\mathrm{B}}P_{\mathrm{Ran}\,\rho}\ln\rho , \tag{13}$$

$$\Delta F = F - \mathrm{Tr}(\rho F)I , \tag{14}$$

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

$$\Gamma(\sqrt{\rho}I, \{\sqrt{\rho}R_i\}) = \Gamma(\{\sqrt{\rho}\Delta R_i\}) = \det[\langle\Delta R_i\Delta R_j\rangle] , \tag{16}$$

where $\Gamma(\{\sqrt{\rho}X_i\})$ denotes the Gram determinant $\det[(\sqrt{\rho}X_i|\sqrt{\rho}X_j)]$.

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

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2k_{\mathrm{B}}\tau(\rho)}\{\Delta M(\rho), \rho\} \tag{17}$$

takes the form

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2k_{\mathrm{B}}\tau(\rho)}\frac{\begin{vmatrix} \{\Delta S, \rho\} & \{\Delta R_1, \rho\} & \cdots & \{\Delta R_i, \rho\} & \cdots \\ & & & & \\ \langle\Delta S\Delta R_1\rangle & \langle\Delta R_1\Delta R_1\rangle & \cdots & \langle\Delta R_i\Delta R_1\rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle\Delta S\Delta R_i\rangle & \langle\Delta R_1\Delta R_i\rangle & \cdots & \langle\Delta R_i\Delta R_i\rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\det[\langle\Delta R_i\Delta R_j\rangle]} . \tag{18}$$

Equations (28) and (29) below show the explicit forms when the set $\{\sqrt{\rho}R_i\}$ is empty or contains only operator $\sqrt{\rho}H$, respectively.

Gheorghiu-Svirschevski [47] re-derived our nonlinear equation of motion from a variational principle that in our notation may be cast as follows [19],

$$\max_{\sqrt{\rho}E_D}\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} \text{ subject to } \frac{\mathrm{d}r_i(\rho)}{\mathrm{d}t} = 0 \text{ and } (\sqrt{\rho}E_D|\sqrt{\rho}E_D) = c^2(\rho) , \tag{19}$$

where $r_0(\rho) = \mathrm{Tr}\rho$, $r_1(\rho) = \mathrm{Tr}H\rho$ [, $r_2(\rho) = \mathrm{Tr}N\rho$], 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

$$\frac{\partial}{\partial \sqrt{\rho} E_D}\frac{\mathrm{d}s}{\mathrm{d}t} - \sum_i \lambda_i \frac{\partial}{\partial \sqrt{\rho} E_D}\frac{\mathrm{d}r_i}{\mathrm{d}t} - \lambda_0 \frac{\partial}{\partial \sqrt{\rho} E_D}(\sqrt{\rho} E_D | \sqrt{\rho} E_D) = 0 \ , \tag{20}$$

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

$$-2k_{\mathrm{B}}(\sqrt{\rho} + \sqrt{\rho}\ln\rho) - 2\sum \lambda_i \sqrt{\rho} R_i - 2\lambda_0 \sqrt{\rho} E_D = 0 \ , \tag{21}$$

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

$$\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} = -k_{\mathrm{B}}\frac{\mathrm{d}\mathrm{Tr}\rho\ln\rho}{\mathrm{d}t} = 4k_{\mathrm{B}}\tau(\rho)\left(\sqrt{\rho} E_D \,|\, \sqrt{\rho} E_D\right) \tag{22}$$

$$= \frac{k_{\mathrm{B}}}{\tau(\rho)}\frac{\Gamma(\sqrt{\rho}\ln\rho, \sqrt{\rho}I, \{\sqrt{\rho}R_i\})}{\Gamma(\sqrt{\rho}I, \{\sqrt{\rho}R_i\})} \tag{23}$$

$$= \frac{1}{k_{\mathrm{B}}\tau(\rho)}\frac{\Gamma(\sqrt{\rho}S, \sqrt{\rho}I, \{\sqrt{\rho}R_i\})}{\Gamma(\sqrt{\rho}I, \{\sqrt{\rho}R_i\})} \geq 0 \ . \tag{24}$$

Because a Gram determinant $\Gamma(\sqrt{\rho}X_1, \ldots, \sqrt{\rho}X_N) = \det[\langle \Delta X_i \Delta X_j \rangle]$ 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

$$\rho = \frac{B\exp[-\beta H\,(+\nu N)]B}{\mathrm{Tr}(B\exp[-\beta H\,(+\nu N)])} \ , \tag{25}$$

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

$$\rho(t) = B(t)\exp[-\beta H\,(+\nu N)]B(t)/\mathrm{Tr}[B(t)\exp[-\beta H\,(+\nu N)]] \ , \tag{26}$$

$$B(t) = U(t)B(0)U^{-1}(t) \ , \quad U(t) = \exp(-itH/\hbar) \ . \tag{27}$$

For $\mathrm{Tr}B = 1$ the states (25) 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 $\rho_{TE} = \exp[-\beta H\,(+\nu N)]/\mathrm{Tr}(\exp[-\beta H\,(+\nu N)])$ 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 $-\mathrm{Tr}\rho\ln\rho$ subject to given values of $\mathrm{Tr}H\rho$ (and $\mathrm{Tr}N\rho$). 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 [35, 48], 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 [49] that the fact that our nonlinear equation of motion preserves the null eigenvalues of ρ, i.e., conserves the cardinality $\dim \mathrm{Ker}(\rho)$ of the set of zero eigenvalues, is an important physical feature consistent with recent experimental tests (see the discussion of this point in Ref. [47] and references 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 [21, 50]. If the Hamiltonian is fully degenerate [$H = eI$, $e(\rho) = e$ for every ρ],

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\tau}\left(\rho \ln \rho - \rho \,\mathrm{Tr}\rho \ln \rho\right) \ , \tag{28}$$

while if the Hamiltonian is nondegenerate,

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

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 [21]

$$\dot{\mathbf{r}} = \omega \mathbf{h} \times \mathbf{r} - \frac{1}{\tau}\left(\frac{1 - r^2}{2r} \ln \frac{1 - r}{1 + r}\right) \frac{\mathbf{h} \times \mathbf{r} \times \mathbf{h}}{1 - (\mathbf{h} \cdot \mathbf{r})^2} \tag{29}$$

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 [21]

$$\frac{\mathrm{d}}{\mathrm{d}t} \ln \frac{1 - r}{1 + r} = -\frac{1}{\tau} \ln \frac{1 - r}{1 + r} \tag{30}$$

which, if τ is constant, has the solution

$$r(t) = \tanh\left[-\exp\left(-\frac{t}{\tau}\right) \ln \frac{1 - r(0)}{1 + r(0)}\right] \ . \tag{31}$$

This, superposed with the precession around the hamiltonian vector, results in a spiraling approach to the maximal entropy state (with entropy $k_\mathrm{B} \ln 2$). 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 $t \to -\infty$ 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 $\mathrm{Tr}\rho$ 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.

XIII.   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 [20]

$$\rho = \frac{B \exp(-\sum_j f_j X_j) B}{\mathrm{Tr} B \exp(-\sum_j f_j X_j)} \; , \tag{32}$$

where the possibly time-dependent Boolean B is such that $B = P_{\mathrm{Ran}\rho} (= I - P_{\mathrm{Ker}\rho})$ 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,

$$\sqrt{\rho}\ln\rho = -f_0\sqrt{\rho} - \sum_j f_j\sqrt{\rho}X_j \; , \tag{33}$$

$$x_j(\rho) = \mathrm{Tr}(\rho X_j) \; , \tag{34}$$

$$s(\rho) = k_{\mathrm{B}}f_0 + k_{\mathrm{B}}\sum_j f_j\,x_j(\rho) \; , \tag{35}$$

$$\text{where} \quad k_{\mathrm{B}}f_j = \left.\frac{\partial s(\rho)}{\partial x_j(\rho)}\right|_{x_{i\neq j}(\rho)} \tag{36}$$

may be interpreted as a "generalized affinity" or force. Defining

$$\frac{\mathrm{D}x_i(\rho)}{\mathrm{D}t} = 2\,(E_D|\,\sqrt{\rho}X_i) \; . \tag{37}$$

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

$$\frac{\mathrm{D}x_i(\rho)}{\mathrm{D}t} = \sum_j f_j\,L_{ij}(\rho) \; , \tag{38}$$

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

$$L_{ij}(\rho) = \frac{1}{\tau(\rho)}\left([\sqrt{\rho}X_i]_{\perp\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})}\,\big|\,[\sqrt{\rho}X_j]_{\perp\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})}\right) \tag{39}$$

$$= \frac{1}{\tau(\rho)}\frac{\begin{vmatrix} \langle\Delta X_i\Delta X_j\rangle & \langle\Delta R_1\Delta X_j\rangle & \cdots & \langle\Delta R_k\Delta X_j\rangle & \cdots \\ \\ \langle\Delta X_i\Delta R_1\rangle & \langle\Delta R_1\Delta R_1\rangle & \cdots & \langle\Delta R_k\Delta R_1\rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \\ \langle\Delta X_i\Delta R_k\rangle & \langle\Delta R_1\Delta R_k\rangle & \cdots & \langle\Delta R_k\Delta R_k\rangle & \cdots \\ \vdots & \vdots & \ddots & \vdots & \ddots \end{vmatrix}}{\det[\langle\Delta R_k\Delta R_\ell\rangle]} = L_{ji}(\rho) \; , \tag{40}$$

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

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

$$\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} = k_{\mathrm{B}}\sum_i\sum_j f_i f_j L_{ij}(\rho) \; . \tag{41}$$

If all operators $[\sqrt{\rho}X_i]_{\perp\mathcal{L}(\sqrt{\rho}I,\{\sqrt{\rho}R_i\})}$ are linearly independent, $\det[L_{ij}(\rho)] \neq 0$ and Eq. (38) may be solved to yield

$$f_j = \sum_i L_{ij}^{-1}(\rho)\frac{\mathrm{D}x_i(\rho)}{\mathrm{D}t} \ , \tag{42}$$

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

$$\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} = k_{\mathrm{B}} \sum_i \sum_j L_{ij}^{-1}(\rho)\frac{\mathrm{D}x_i(\rho)}{\mathrm{D}t}\frac{\mathrm{D}x_j(\rho)}{\mathrm{D}t} \ . \tag{43}$$

XIV.   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 $H = \sum_{J=1}^{r}(H_1)_J \otimes I_{\overline{J}} + V$ 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, $J = 1,\ldots,r$, 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 $H = \sum_{J=1}^{r} I_{\overline{J}} \otimes \sum_{n_J=0}^{\infty} H_{n_J} P_{\mathcal{H}_{d_J}^{\otimes n_J}} + V$.

For compactness of notation we denote the subsystem Hilbert spaces as

$$\mathcal{H} = \mathcal{H}^1\otimes\mathcal{H}^2\otimes\cdots\otimes\mathcal{H}^r = \mathcal{H}^J\otimes\mathcal{H}^{\overline{J}} \ , \tag{44}$$

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

$$H = \sum_{J=1}^{r} H_J\otimes I_{\overline{J}} + V \ , \tag{45}$$

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 [18, 19, 46] to implement the steepest entropy ascent ansatz in a way compatible with the obvious self-consistency "separability" and "locality" requirements [49]. 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 [18, 46] so as to guarantee all the necessary features (that we list in Ref. [49]), is

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = -\frac{i}{\hbar}[H,\rho] + \sum_{J=1}^{r}\frac{1}{2k_{\mathrm{B}}\tau_J(\rho)}\{(\Delta M_J(\rho))^J,\rho_J\}\otimes\rho_{\overline{J}} \ , \tag{46}$$

where we use the notation [see Ref. [19] for interpretation of $(S)^J$ and $(H)^J$]

$$\sqrt{\rho_J}(M_J(\rho))^J = \left[\sqrt{\rho_J}(S)^J\right]_{\perp\mathcal{L}(\sqrt{\rho_J}I_J,\sqrt{\rho_J}(H_J)^J(,\sqrt{\rho_J}(N_{kJ})^J))} \ , \tag{47}$$

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

$$(R_{iJ})^J = \mathrm{Tr}_{\overline{J}}[(I_J\otimes\rho_{\overline{J}})R_{iJ}] \ , \tag{49}$$

$$(S)^J = \mathrm{Tr}_{\overline{J}}[(I_J\otimes\rho_{\overline{J}})S] \ , \tag{50}$$

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

$$\frac{\mathrm{d}s(\rho)}{\mathrm{d}t} = \sum_{J=1}^{r} \frac{1}{k_{\mathrm{B}}\tau_J(\rho)} \frac{\Gamma(\sqrt{\rho_J}(S)^J, \sqrt{\rho_J}I_J, \{\sqrt{\rho_J}(R_{iJ})^J\})}{\Gamma(\sqrt{\rho_J}I_J, \{\sqrt{\rho_J}(R_{iJ})^J\})} \ . \tag{51}$$

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

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

The equivalent variational formulation is

$$\max_{\{\sqrt{\rho_J}E_{DJ}\}} \frac{\mathrm{d}s(\rho)}{\mathrm{d}t} \text{ subject to } \frac{\mathrm{d}r_i(\rho)}{\mathrm{d}t} = 0 \text{ and } (\sqrt{\rho_J}E_{DJ}|\sqrt{\rho_J}E_{DJ})_J = c_J^2(\rho) \ , \tag{53}$$

where $r_0(\rho) = \mathrm{Tr}\rho$, $r_1(\rho) = \mathrm{Tr}H\rho$ [, $r_2(\rho) = \mathrm{Tr}N\rho$], 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

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

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

where $(\rho_A)_{\overline{J}} = \mathrm{Tr}_J(\rho_A)$, $(\rho_B)_{\overline{J}} = \mathrm{Tr}_J(\rho_B)$, 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.

XV. 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 [11, 48] 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 [48] about the QSM/QIT interpretation of density operators, which has preoccupied scientists and philosophers since when Schrödinger surfaced it in Ref. [4]. This fundamental ansatz seems to respond to Schrödinger prescient conclusion in Ref. [4]: "...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" [52], 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 [51], 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 [51] "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" [2, 32, 46] 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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[13] Ref. [7], p. xvii.

[14] Ref. [7], p. 165.

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