QUANTUM THERMODYNAMICS:
MICROSCOPIC FOUNDATIONS OF ENTROPY
AND OF MAXIMAL ENTROPY GENERATION BY IRREVERSIBILITY

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ABSTRACT

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?

Most physicists still accept and teach that the rationalization of these fundamental questions is given by Statistical Mechanics. Indeed, 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 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 we call Quantum Thermodynamics, 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 nonequilibrium dynamics.

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 that 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.

In this paper we discuss the background and formalism of Quantum Thermodynamics including its nonlinear equation of motion and the main general results. Our objective is to show in a not-too-technical manner that this theory provides indeed a complete and coherent resolution of the century-old dilemma on the meaning of entropy and the origin of irreversibility, including Onsager reciprocity relations and maximal-entropy-generation nonequilibrium dynamics, which we believe provides the microscopic foundations of heat, mass and momentum transfer theories, including all their implications such as Bejan's Constructal Theory of natural phenomena.

1 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 vaste 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 MIT school 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 MIT school about twenty years ago (and still only partly recognized by the orthodox physical community, see Ref. 18).

Even though Quantum Thermodynamics is based on conceptual premises that are indeed quite revolutionary and entirely different from those of Statistical Mechanics, we cannot overemphasize that the new theory retains the whole mathematical formalism of Statistical Mechanics – 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 questions and opens new vistas on the fundamental description of nonequilibrium, offering a powerful general equation for irreversibile dynamics.

2 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.[6]

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.

2.1 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.

2.2 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 of 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 annull 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.

2.3 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.[6]

3 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.

3.1 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,

$$\mathcal{H} = \mathcal{H}^1 \otimes \mathcal{H}^2 \otimes \cdots \otimes \mathcal{H}^M \qquad (1)$$

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*

$$\frac{d\psi}{dt} = -\frac{i}{\hbar} H\psi \ . \qquad (2)$$

Because the solution of the Schrödinger equation can be written as

$$\psi(t) = U(t)\psi(0) \ , \qquad (3)$$

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

$$U(t) = \exp(-itH/\hbar) \ , \qquad (4)$$

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

3.2 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,[7] 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

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

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

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

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

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

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

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

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.

3.3 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 $P_\psi = |y\rangle\langle y|$, 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 $-k_B \, \text{Tr} \rho \ln \rho$ and, therefore, the "entropy" is an invariant of the endogenous dynamics.

Here the problem becomes delicate. On the one hand, the "entropy" functional $-k_B \, \text{Tr} \rho \ln \rho$ 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[8] 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 increa-
se spontaneously as a result of an irreversible process, is
confronted with the invariance of the "entropy" functio-
nal $-k_B \operatorname{Tr}\rho \ln \rho$ under unitary dynamics. This leads to
the conclusion (within Statistical Mechanics) that entropy
generation by irreversibility cannot be a result of the endo-
genous 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.

4 TOWARDS A BETTER THEORY

For a variety of ad-hoc reasons – statistical, phenome-
nological, information- theoretic, quantum-theoretic, con-
ceptual – many investigators have concluded that the von
Neumann equation of motion (Equation 11) is incomple-
te, and a number of modification have been attempted.[9]
The attempts have resulted in ad-hoc tools valid only for
the description of specific problems such as, e.g., the none-
quilibrium dynamics of lasers. However, because the un-
derlying conceptual framework has invariably been that
of Statistical Mechanics, none of these attempts has re-
moved 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 ap-
proach:[8] that of constructing a functional for the entro-
py, 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 intro-
ducing 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 supe-
roperator $L \cdot = [H, \cdot]/\hbar$ and such that the von Neumann
equation for ρ, $d\rho/dt = -iL\rho$, induces an equation of mo-
tion 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 wi-
th 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, ca-
pable 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 gra-
dually adopted a new important element with growing con-
viction: the idea that entropy is a microscopic quantity
and that irreversibility should be incorporated in the mi-
croscopic description. However, credit for this new and
revolutionary idea, as well as its first adoption and cohe-
rent implementation, must be given to the pioneers of the
MIT school,[10] even though the Brussels school might ha-
ve 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 re-
cent discussion on quantum entaglement and separability,

relevant to understanding and predicting decoherence in
important future applications involving nanometric devi-
ces, fast switching times, clock synchronization, superden-
se coding, quantum computation, teleportation, quantum
cryptography, etc, the question of the existence of "sponta-
neous decoherence" at the microscopic level is emerging as
a fundamental test of standard Quantum Mechanics[18].

As we will see, the implementation proposed by the MIT
school has provided for the first time an alternative to Sta-
tistical Mechanics capable of retaining all the successful
aspects of its formalism within a sound conceptual fra-
mework 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 phy-
sical thought as the concept of trajectory and the principle
of causality.

5 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[10] concluded that the state
domain of Quantum Mechanics is too small to include all
the states that a physical system can assume. Indeed, the
entire body of results of Quantum Mechanics has been so
successful in describing empirical data that it must be re-
tained 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 in-
terpretation. In other words, all that matters is to retain
the mathematical formalism, freeing it from its troubleso-
me statistical interpretation.

The great discovery was that all this can be achieved if
we admit that *physical systems have access to many mo-
re states than those described by Quantum Mechanics* and
that the set of states is in one-to-one correspondence wi-
th the set of self-adjoint, nonnegative-definite, unit-trace
linear operators ρ on the same Hilbert space $\mathcal{H}$ that Quan-
tum Mechanics associates with the system (mathemati-
cally, 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 conside-
red in Quantum Mechanics are only the extreme points of
the set of states a system really admits.

In terms of interpretation, the conceptual inconsisten-
cies inherent in Statistical Mechanics are removed. The
state operators ρ are mathematically identical to the den-
sity operators of Statistical Mechanics, but now they repre-
sent true states, in exactly the same way as a state vector
ψ represents a true state in Quantum Mechanics. Stati-
stics 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

State domain in standard
Quantum Mechanics

State domain in
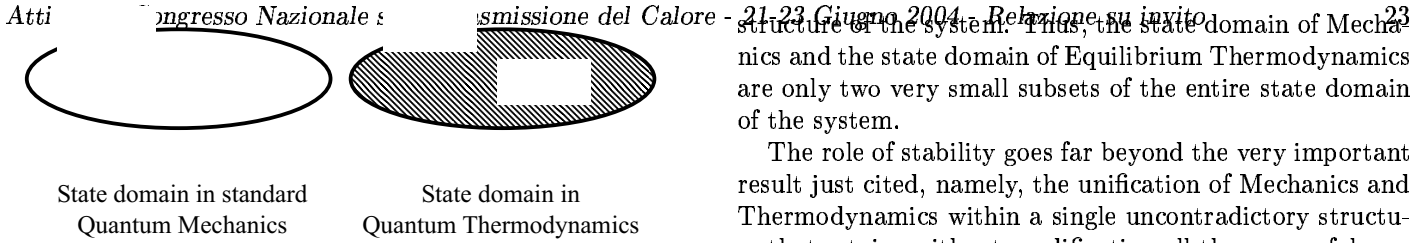Quantum Thermodynamics

Figure 1: Pictorial representation of the augmented state domain implied by the Hatsopoulos-Gyftopoulos kinematics with respect to the state domain of standard Quantum Mechanics.

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.

6   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.[5-6] 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.[10] 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.

7   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:[11] "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:[12] "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 $\mathrm{Tr} H \rho$ 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 $\mathrm{Tr} N \rho$ 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 $\mathrm{Tr} N_i \rho$ 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 $\mathrm{Tr}(H_A \otimes I_B)\rho$ and $\mathrm{Tr}(I_A \otimes H_B)\rho$ 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 $\rho_A = \mathrm{Tr}_B \rho$, $\rho_B = \mathrm{Tr}_A \rho$, 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 $\mathrm{Tr} H \rho$ and the number-of-particle functionals $\mathrm{Tr} N_i \rho$ (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 $-k_B \, \mathrm{Tr} \rho \ln \rho$ along every trajectory must be nonnegative.

It is clear that with all these conditions[22] 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.

8 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][10] (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 enviromment. 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.
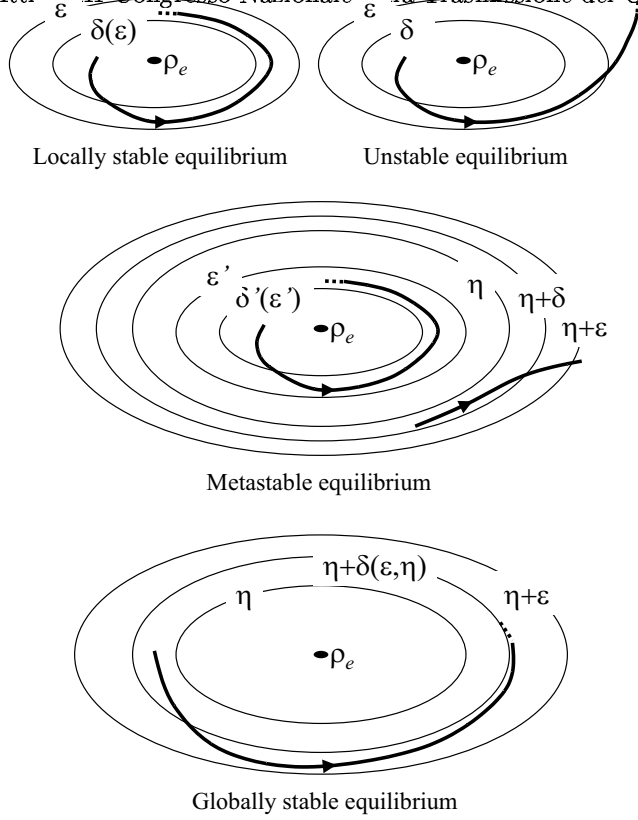
Figure 2: Technical definitions of stability of equilibrium. Thermodynamic equilibrium states are globally stable.

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 $\mathrm{Tr} H\rho$ and $\mathrm{Tr} N_i \rho$ (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.

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[13] 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. 13 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[13] 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[14] "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.

9 THE DYNAMICAL POSTULATE OF QUANTUM THERMODYNAMICS

Let us summarize briefly the elements of Quantum Thermodynamics that we have already discussed. With every system is associated a Hilbert space $\mathcal{H}$, the same $\mathcal{H}$ that is associated with the system in Quantum Mechanics. The composition of the system in terms of distinguishable subsystems is reflected by the structure of the Hilbert space $\mathcal{H}$ as a direct product of subspaces. The subdivision into constituents, considered as indivisible, is particularly im-

portant because it defines the level of description of the system and specifies its elementary structure. This will determine also the structure of the dynamical law.

With the state of the system is associated a state operator ρ, i.e., a self-adjoint, nonnegative-definite, unit-trace linear operator on $\mathcal{H}$. If the state operator is idempotent, i.e., $\rho^2 = \rho$, then ρ is a one-dimensional projector onto the linear span of some vector ψ in $\mathcal{H}$, i.e., $\rho = P_\psi$, and corresponds to a *mechanical state*, i.e., a state of Quantum Mechanics. If ρ is not idempotent then it corresponds to a *nonmechanical state*, i.e., a state not contemplated by Quantum Mechanics. Again, we emphasize that a unique and key premise of Quantum Thermodynamics is that in addition to the states of Quantum Mechanics a system (even if strictly uncorrelated and isolated from the rest of the universe) has access also to states that must be described by nonidempotent state operators. Among these nonmechanical states are, for example, those expressed in terms of functions of the Hamiltonian and the number-of-particle operators in Equations 5 to 7.

The functional representing the *entropy* is $-k_B \operatorname{Tr}\rho\ln\rho$. It represents a property of matter in the same sense as the energy functional $\operatorname{Tr}H\rho$ represents a property of matter. Entropy can be interpreted as a measure of the breadth of the irreducible indeterminacy inherent in the states represented by nonidempotent state operators. This indeterminacy is added on top of that implied by the Heisenberg uncertainty principle, and is responsible, for example, of the impossibility of adiabatic extraction of energy from the states of Equilibrium Thermodynamics (impossibility of perpetual motion of the second kind).

If a constituent is part of a system with other constituents, its state may be correlated or uncorrelated from the rest of the system. Considering a system composed of M distinguishable constituents, the Hilbert space $\mathcal{H} = \mathcal{H}^J \otimes \mathcal{H}^{\overline{J}}$ where $\mathcal{H}^J$ is the Hilbert space associated with the J-th constituent of the system, and $\mathcal{H}^{\overline{J}}$ that associated with the rest of the system. We say that constituent J is uncorrelated from the rest of the system if the state operator $\rho = \rho_J \otimes \rho_{\overline{J}}$ where $\rho_J = \operatorname{Tr}_{\overline{J}}\rho$ and $\rho_{\overline{J}} = \operatorname{Tr}_J\rho$, $\operatorname{Tr}_{\overline{J}}$ denotes the partial trace over $\mathcal{H}^{\overline{J}}$ and Tr_J the partial trace over $\mathcal{H}^J$.

The most general way to represent a constituent is in terms of a field consisting of variable amounts of all the n types of particles present in the overall system. For the J-th constituent considered as isolated, we denote the Hamiltonian operator on $\mathcal{H}^J$ by $H(J)$, the number-of-particles-of-i-th-type operator by $N_i(J)$ and the identity operator by $I(J)$. The Hamiltonian H of the overall system, including the interaction term, is given by Equation 8 and the overall-number-of-particles-of-i-th-type operator N_i by Equation 9. To simplify the notation, and without loss of generality, we assume that all the constituents of the system are of this general kind. Then, for example, we can specify that, say, the K-th constituent consists of only the 4-th type of particle with variable amount by imposing that $N_i(K)$ is the null operator for every $i \neq 4$. Again, if the K-th constituent consists of only the 2-nd type of particle with a fixed amount, say, 5 particles, then $N_i(K) = 0$ for $i \neq 2$ and $N_2(K) = 5I(K)$.

The dynamical law proposed by the present author to complete Quantum Thermodynamics[15] is given by the following general equation of motion, which satisfies all the Conditions 1 to 6 listed above,

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \sum_{J=1}^{M} \frac{1}{2\tau_J(\rho)}\left(\sqrt{\rho_J}D_J + (\sqrt{\rho_J}D_J)^\dagger\right) \otimes \rho_{\overline{J}}$$

(14)

where $\tau_J(\rho)$ is a positive internal-dissipation time functional (or constant) of constituent J, $X^\dagger$ denotes the adjoint of operator X, and the operators D_J are defined as follows

$$D_J = \sqrt{\rho_J}(B\ln\rho)^J - (\sqrt{\rho_J}(B\ln\rho)^J)_{\mathcal{L}} ,$$

(15)

where

$$(B\ln\rho)^J = \operatorname{Tr}_{\overline{J}}[(I(J) \otimes \rho_{\overline{J}})B\ln\rho] ,$$

(16)

$$(H)^J = Tr_{\overline{J}}[(I(J) \otimes \rho_{\overline{J}})H] ,$$

(17)

and

$$(\sqrt{\rho_J}(B\ln\rho)^J)_{\mathcal{L}}$$

(18)

denotes the orthogonal projection of operator $\sqrt{\rho_J}(B\ln\rho)^J$ onto the linear span

$$\mathcal{L}[\sqrt{\rho_J}, \sqrt{\rho_J}(H)^J, \sqrt{\rho_J}N_1(J), \ldots, \sqrt{\rho_J}N_n(J)]$$

of operators $\sqrt{\rho_J}$, $\sqrt{\rho_J}(H)^J$, $\sqrt{\rho_J}N_1(J)$, $\ldots$, $\sqrt{\rho_J}N_n(J)$, with respect to the scalar product on the set of linear operators on $\mathcal{H}^J$ defined by $(F, G) = (1/2)\operatorname{Tr}_J(F^\dagger G + G^\dagger F)$. Operator B is idempotent ($B^2 = B$) and is obtained from the spectral expansion of the state operator ρ by substituting each nonzero eigenvalue of ρ with unity, so that $\operatorname{Tr}B$ equals the number of nonzero eigenvalues of ρ and $B\ln\rho$ is a well-defined operator with eigenvalues that are either zero or the logarithm of the nonzero eigenvalues of ρ. We denote by $B\mathcal{H}$ the subspace of $\mathcal{H}$ spanned by the "occupied" eigenvectors of ρ, i.e., the eigenvectors corresponding to nonzero eigenvalues.

Equation 14 is well-defined over the entire state domain. More explicit expressions of the operators D_J are given in Refs. 15 and 23 where, among many other results, it is shown that indeed Conditions 1 to 6 are satisfied. We call the first term in the right-hand side of Equation 14 the *Hamiltonian term* and the second term the *dissipative term*.

Despite its apparent complexity, the form of the equation of motion is geometrically simple and unique in that the dissipative term identifies the direction (in state domain) of highest entropy ascent[19]. The important effect of the dissipative term is to alter the nonzero eigenvalues of ρ until the highest entropy (partially) canonical or grand-canonical distribution is reached, compatible with the initial values of the energy functioanl, the number-of-particles functionals, and the cardinality of the zero eigenvalues, which remain invariant. Recently, Gheorghiu-Svirschevski[18] "rediscovered" the equation of motion for the single constituent case by deriving it from an equivalent variational-principle formulation (which can be readily extended to the multi-constituent case[23]), and obtained an interesting general near-equilibrium linearization.

The Hamiltonian term of the equation of motion tends to generate a reversible unitary evolution which, as we know, would maintain the trajectory on a constant entropy surface in the state domain. The dissipative term tends to generate an irreversible evolution by "pulling" the state operator towards the local direction (in the state domain)
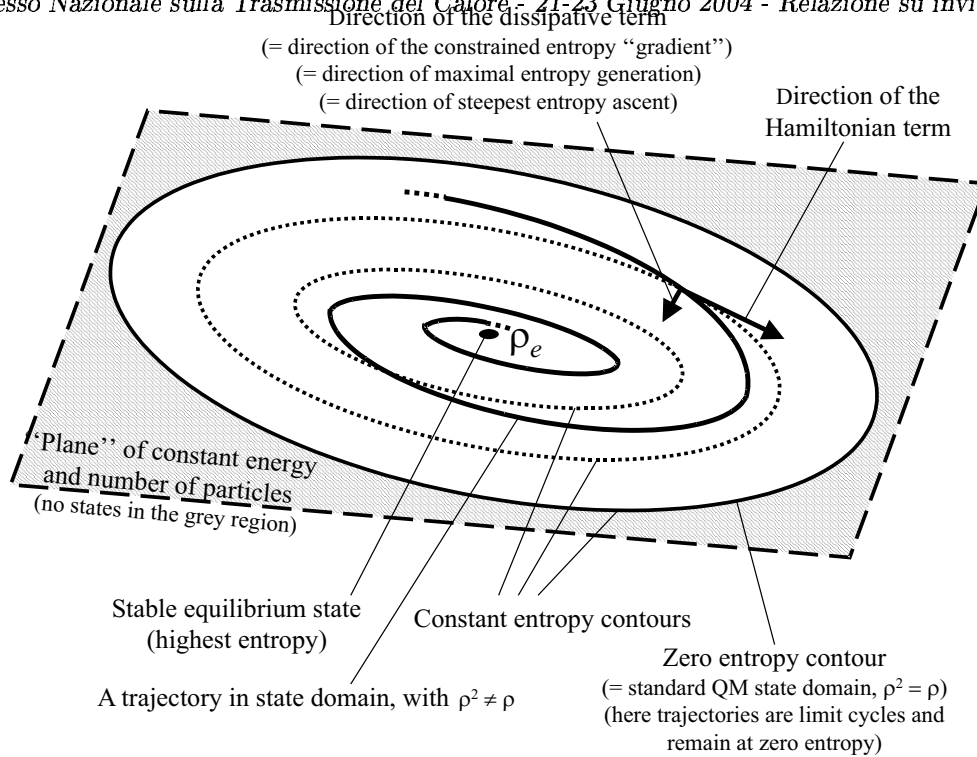
Figure 3: Pictorial representation of a trajectory in the region of the augmented state domain where $\rho^2 \neq \rho$, showing that the motion results from the combined action of the Hamiltonian term and the dissipative term in the equation of motion of Quantum Thermodynamics. Where $\rho^2 = \rho$, the entropy and the dissipative term are zero, and the motion is driven only by the Hamiltonian term and results in the usual periodic unitary evolution of standard Quantum Mechanics. The picture assumes that ρ has no zero eigenvalues or, equivalently, the Hilbert space is restricted to $B\mathcal{H}$.

of steepest entropy ascent compatible with the conditions on the time invariants and the structure of the system, i.e., equivalently, the direction of maximal local entropy generation or, which is the same, the direction of the local entropy "gradient" with respect to state domain coordinates.

In view of its nonlinearity in the state operator ρ, the "strength" of the dissipative term depends not only on the internal-dissipation time $\tau_J(\rho)$ but most importantly on the instantaneous location of the state operator in the state domain. The actual evolution results from the competition of the Hamiltonian and the dissipative terms.

For a system consisting of a single constituent, the equation of motion is clearly simplified. Then, as illustrated in Figure 3, the dissipative term pulls the state ρ exactly in the direction of steepest ascent of $-k_B \operatorname{Tr}\rho \ln \rho$ compatible with the invariance of $\operatorname{Tr}\rho$, $\operatorname{Tr}N_i\rho$, $\operatorname{Tr}H\rho$, and the zero eigenvalues and eigenvectors of ρ.

For a system with many constituents, the functionals $\operatorname{Tr}_J(H)^J\rho_J$ and $-k_B \operatorname{Tr}_J\rho_J(B\ln\rho)^J$ represent a sort of "local perception" by the J-th constituent of the overall energy and entropy of the system. The structure of the dissipative term is such that each constituent contributes according to its own local attraction towards the direction of steepest locally perceived entropy ascent, namely, the direction of projection of the gradient of the functional $-k_B \operatorname{Tr}_J\rho_J(B\ln\rho)^J$ onto the local "plane" of constant values of the functionals $\operatorname{Tr}_J\rho_J$, $\operatorname{Tr}_JN_i(J)\rho_J$, and $\operatorname{Tr}_J(H)^J\rho_J$, i.e., the local perception of the overall system invariants (unit trace, energy and number of particles).

The explicit form of the equation for a single constituent

consisting of a single two-level atom or spin is discussed in Ref. 16. In Ref. 17 we establish corrections implied by our equation of motion onto the basic quantum-electrodynamic results on resonance fluorescence and stimulated emission.

In Figure 4 we reproduce the noteworthy comment by the Editor of Nature magazine published immediately after publication of the articles in Ref. 15.

The nonlinearity of the dissipative term and the singularity of operator $B\ln\rho$ guarantee at the level of the individual dynamics of each constituent of matter a great richness of dynamical features which, together with the complexity of structure for a system with many distinguishable constituents, can certainly produce the wealth of nonequilibrum conditions and self-organization behavior sought by the Brussels school.

10   ORIGIN AND GENERALIZATION OF ONSAGER RECIPROCAL RELATIONS

Another important question that is resolved by Quantum Thermodynamics is related to the general description of nonequilibrium states and their time evolution. We have seen that the states of Quantum Mechanics and those of Equilibrium Thermodynamics constitute very small subsets of the state domain of Quantum Thermodynamics. With the exception of a relatively small number of equilibrium states that are not globally stable,[15] all the other states are nonequilibrium.

An interesting way to represent a general state operator,

NEWS AND VIEWS

Uniting mechanics and statistics

An adventurous scheme which seeks to incorporate thermodynamics into the quantum laws of motion may end arguments about the arrow of time — but only if it works.

THE logical relationship between the laws of mechanics and those of thermodynamics deserves more attention than it usually receives. Thermodynamics and statistical mechanics are ways of describing the behaviour of macroscopic systems made from components whose behaviour is determined by the laws of mechanics, classically those of Newton (as amended), but otherwise the equations of motion of quantum mechanics. Where the first law of thermodynamics is concerned, there is no difficulty. In both classical and quantum mechanics, total energy is a constant of the motion and is thus always conserved, at least in a closed system.

The difficulty arises chiefly with the second law of thermodynamics, and not only because there is such a variety of ways in which this principle can be defined. But now a group of three theoreticians has put forward an intriguing way in which the laws of quantum mechanics may be modified so as to incorporate the second law from what appears to be the outset (Beretta, G. P., Gyptopoulos, E. P. & Park, J. L., *Il Nuovo Cimento B* 87, 77–97; 1985). Whether the modification proposed is sufficient, only time will tell, but the objective seems well worth the trouble Beretta *et al.* have taken.

The difficulty is well illustrated by the way in which some kind of correspondence is established between the mechanical behaviour of a system and its thermodynamic properties. For more than a century, people have been brooding on the paradox that while the laws of classical (and, for that matter, quantum) mechanics are symmetrical with respect to time inversion, the second law selects from all possible trajectories of motion only those corresponding to a continual increase of the entropy. The arrow of time is conjured like a rabbit from a hat.

The definition of entropy in terms of the mechanical properties of the constituents of a system is similarly clouded. The classical model is Boltzmann's *H*-theorem (1872), which shows that the rate of change with time of a certain mathematical construct from the probability distribution of single particles in phase space will always be zero or negative. So Boltzmann argued, his quantity *H* is admirably suited to be the negative of what is known in thermodynamics as entropy. This is argument by analogy, but none the worse for that — if it works.

Since Boltzmann's time, there has accumulated a rich literature on the implied paradox of the conflict between the irreversibility of macroscopic processes and the reversibility (in time) of the laws of mechanics and thus of microscopic processes. Indeed, the argument was begun by Loschmidt in 1976, but now even elementary text-books of thermodynamics reckon to give some kind of account of it.

The standard explanation is that the apparent paradox is not a paradox at all, but a confusion about timescales. Any measure of entropy, that derived from Boltzmann's *H* or otherwise, will fluctuate (and so decrease as well as increase on a short timescale), which is not inconsistent with the notion that the average value of the entropy should increase steadily over long periods of time (or remain unchanged when the system is in equilibrium).

Much the same is said of the recurrence paradox, based on the observation due to Poincaré that the point in phase space (momentum as well as position) representing the state of a classical system will return to more or less the same place after a sufficient length of time. On the face of things, that means that non-equilibrium states of a system will repeatedly recur. The standard resolution of that paradox is the observation that, for any realistic system, the interval of time between recurrences will be huge, much greater than, say, the age of the Universe. Again there is nothing wrong with these arguments, but they are far from being rigorous.

So why not take the bull by the horns, and build irreversibility into the laws of mechanics? That is the point from which Beretta *et al.* start. Properly, they acknowledge that they are not the first to tread this path. They work with quantum statistical mechanics, where the formalism is easier. They start from the equation of motion for the operator representing the state of a physical system, say m, which is, in operator language, $dm/dt = -i/\hbar[H,m]$, where *t* is time, H the Hamiltonian operator of the system and *i* and $\hbar$ the square route of minus once and Planck's constant (divided by 2π) respectively. The quantity in square brackets is the commutator of its two components, mH — Hm.

The natural way to proceed is to assume that this equation is modified in such a way that the right-hand side is some other function of the state operator m than in the standard form. The objective is to find a form of the function which is compatible both with what is known of the evolution of thermodynamic systems and, perhaps more important, the dynamics of real microscopic systems. Beretta *et al.* have convinced themselves that the function they are seeking cannot be a linear function of m. What they propose is the addition to the right-hand side of the quantum equation of motion of a particular function of m which, by including both the square root and the logarithm of the state operator of the system, is non-linear enough to satisfy anybody's taste.

Almost magically, the system has some of the obviously necessary properties. For example, for a system in a pure quantum state, say that represented by a solution of Schrodinger's equation, the extra terms vanish and the simple form of the equation of motion applies. Similarly, constants of the motion in the new system are also constants of the motion determined by the simpler equation of motion.

What can be said about the entropy? In reality, the state operator m is the equivalent of what is called the density matrix in quantum statistical mechanics, which is why Beretta *et al.* define entropy in terms of the operator mlogm, where the logarithm is the natural logarithm of the operator m. Specifically, the entropy of the negative of the trace of this operator multiplied by Boltzmann's constant; the authors are able to show that is increases (or does not increase) in the course of time.

So is this a demonstration that the laws of mechanics and of thermodynamics can indeed be combined? Not quite. For one thing, there are various mathematical problems that make some of the steps in the argument conjectural. Worse still, some of the operator functions in the formalism are sometimes undefined. But the system does have the merit of hanging together — the paper now published extends to composite systems the treatment of one-component systems published a year ago.

None of this implies that the arguments about the reconciliation between microscopic reversibility and macroscopic ir reversibility will now be stilled. Indeed, while for as long as the present justification of the basis of statistical mechanics holds water, there will be many who say that what Beretta *et al.* have done is strictly unnecessary. But this is a field in which the proof of the pudding is in the eating.

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Figure 4: Reproduction (with permission) of a Nature magazine editorial comment on our articles in Ref. 15.

equilibrium or nonequilibrium, is in terms of a fixed set of operators X_1, X_2, ..., X_i, ... that span the real space of self-adjoint linear operators on $\mathcal{H}$. We can write any state operator as[19]

$$\rho = \frac{B \exp(-\sum_i f_i X_i / k_B)}{\mathrm{Tr}[B \exp(-\sum_i f_i X_i / k_B)]} \qquad (19)$$

where f_1, f_2, ..., f_i, ... are real scalars and B is an idempotent self-adjoint operator. The main and most important difference between Equation 19 and Equations 5 to 7 is that the list of operators X_i must be *complete* in the sense that any other self-adjoint operator on $B\mathcal{H}$ can be expressed as a linear combination of the X_i's. In general, $\dim B\mathcal{H} = \infty$ and the list of X_i's is infinite, however, for finite dimensional $B\mathcal{H}$ (states with a finite number of occupied eigenvectors) the set of X_i's is finite.

In terms of Equation 19, the entropy functional becomes a linear combination of the functionals $\mathrm{Tr}X_i\rho$, i.e.,

$$-k_B \mathrm{Tr}\rho \ln \rho = \sum_i f_i \mathrm{Tr}X_i\rho \qquad (20)$$

so that the scalar f_i can be interpreted as a *generalized "affinity"* or *"force"* representing the marginal dependence of the entropy functional on the change in value of the property represented by functional $\mathrm{Tr}X_i\rho$.

It is then interesting to evaluate the rate of change of $\mathrm{Tr}X_i\rho$ as due to the equation of motion (Equation 14), specifically, to the dissipative term of the equation of motion. We know that the Hamiltonian term cannot alter the value of the entropy. Therefore, we focus our attention on the contribution of the dissipative term, that we denote by $D\mathrm{Tr}X_i\rho/Dt$ and call the *dissipative rate of change* of the property represented by the functional $\mathrm{Tr}X_i\rho$.

Substituting the explicit expression of the dissipative term,[19] we find

$$\frac{D\mathrm{Tr}X_i\rho}{Dt} = \sum_i f_i L_{ij}(\rho) \qquad (21)$$

and

$$-k_B \frac{d}{dt}\mathrm{Tr}\rho \ln \rho = \sum_i f_i \frac{D\mathrm{Tr}X_i\rho}{Dt} = \sum_i \sum_j f_i f_j L_{ij}(\rho) \qquad (22)$$

where

$$L_{ij}(\rho) = \sum_{J=1}^{M} \frac{1}{k_B \tau_J} \left((\sqrt{\rho_J}(X_i)^J)_{\perp \mathcal{L}}, (\sqrt{\rho_J}(X_j)^J)_{\perp \mathcal{L}} \right) = L_{ji}(\rho) \qquad (23)$$

$$(X_i)^J = Tr_{\overline{J}}[(I(J) \otimes \rho_{\overline{J}})X_i] \qquad (24)$$

$$(\sqrt{\rho_J}(X_j)^J)_{\perp \mathcal{L}} = \sqrt{\rho_J}(X_j)^J - (\sqrt{\rho_J}(X_j)^J)_{\mathcal{L}} \qquad (25)$$

$(\cdot, \cdot)$ denotes the scalar product $(F, G) = (1/2)\mathrm{Tr}_J(F^\dagger G + G^\dagger F)$, and $(\sqrt{\rho_J}(X_i)^J)_{\mathcal{L}}$ denotes the orthogonal projection of operator $\sqrt{\rho_J}(X_i)^J$ onto the linear span $\mathcal{L}$ of operators $\sqrt{\rho_J}$, $\sqrt{\rho_J}(H)^J$, $\sqrt{\rho_J}N_1(J)$, ..., $\sqrt{\rho_J}N_n(J)$.

In view of Equation 21, the functional $L_{ij}(\rho)$ can be interpreted as a *generalized "conductivity"* expressing the linear dependence of the dissipative rate of change of the i-th functional $\mathrm{Tr}X_i\rho$ on the j-th affinity f_j. The conclusion that $L_{ij}(\rho) = L_{ji}(\rho)$, implies that at every state ρ, the marginal dependence of the dissipative rate of change of the i-th functional $\mathrm{Tr}X_i\rho$ on changes in value of the j-th affinity f_j is equal to the marginal dependence of the dissipative rate of change of the j-th functional $\mathrm{Tr}X_j\rho$ on changes in value of the i-th affinity f_i. This conclusion represents a proof of Onsager's reciprocity relations expressing the reciprocity of the mutual interrelations between different irreversible rate phenomena simultaneously occurring at a nonequilibrium state.

Onsager's result[20] was obtained from empirical observations on nonequilibrium phenomena very close to stable thermodynamic equilibrium, so that the list of X_i's was indeed very short, and the result valid only for a limited class of states. Our result[19] generalizes the validity of Onsager's reciprocity relations (as well as Callen's fluctuation-dissipation relations) to all nonequilibrium states, close and far from stable thermodynamic equilibrium. Of course, the price we have to pay to describe nonequilibrium states far from stable equilibrium is that we *must* use a much larger, possibly infinite list of X_i's.

11   CONCLUSION

All the results summarized in this article unfold from the recognition of the role played by stability in Thermodynamics.[5-6][10][13][15]

In our view, Quantum Thermodynamics constitutes the first self-consistent and conceptually sound resolution of the century-old dilemma on the nature of entropy and irreversibility.

While encompassing all the successful results of Quantum Mechanics, Equilibrium Thermodynamics, and the formalism of Statistical Mechanics, it opens new vistas towards a unifying reexamination of nonequilibrium phenomena.

Its maximal-entropy-generation nonlinear dynamical principle provides an all-encompassing microscopic foundation of nonequilibrium phenomena, of Onsager reciprocity and Callen dissipation-fluctuation relations, and therefore of heat, mass and momentum transfer theories.

Maximal entropy generation at the microscopic level Bejan's Constructal Theory of natural phenomena.

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21. Without loss of generality, we restrict our discussion to an uncorrelated and noninteracting system, i.e., a strictly isolated system. The argument that "real" systems are not isolated is irrelevant to our discussion because here we are concerned with what is conceivable within a physical theory, and there would be no ground for any physical theory if isolated systems were not conceivable.

22. For a more detailed, technical and complete set of conditions, including those related to the more recent discussions on strong separability and entanglement, see G.P. Beretta, arXiv: quant-ph/0402108 (2004).

23. For a more detailed, technical and complete review of quantum thermodynamics, see G.P. Beretta, arXiv: quant-ph/0112046 (2001) and references therein.