INTRINSIC ENTROPY AND INTRINSIC IRREVERSIBILITY FOR A SINGLE ISOLATED CONSTITUENT OF MATTER: BROADER KINEMATICS AND GENERALIZED NONLINEAR DYNAMICS

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INTRODUCTION

What if entropy, rather than a statistical, information theoretic, macroscopic or phenomenological concept, were an intrinsic property of matter in the same sense as energy is universally understood to be an intrinsic property of matter? What if irreversibility were an intrinsic feature of the fundamental dynamical laws obeyed by all physical objects, macroscopic and microscopic, complex and simple, large and small? What if the second law of thermodynamics, in the hierarchy of physical laws, were at the same level as the fundamental laws of mechanics, such as the great conservation principles? Is it inevitable that the gap between mechanics and thermodynamics be bridged by resorting to the usual statistical, phenomenological, or information-theoretic reasoning, and by hinging on the hardly definable distinction between microscopic and macroscopic reality? Is it inevitable that irreversibility be explained by designing ad hoc mechanisms of coupling with some heat bath, reservoir or environment, and ad hoc mechanisms of loss of correlation? What if, instead, mechanics and thermodynamics were both special cases of a more general unified fundamental physical theory valid for all systems, including a single strictly isolated particle, such as a single isolated harmonic oscillator or a single isolated two-level spin system?

In spite of a century of inquiries, scrutinies, claims, proposals and conjectures, we can still venture no definitive answers to these profound unresolved fundamental physical questions. However, we can show that it is possible to construct a logically consistent, mathematically sound and definite, physically intriguing and appealing, nonstatistical unified quantum theory encompassing

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both quantum mechanics and thermodynamics as special cases. In this unified quantum theory, that we call Quantum Thermodynamics, entropy emerges as an intrinsic property of matter, irreversibility emerges as an intrinsic feature of the individual internal dynamics of each constituent of matter, and the second law of thermodynamics emerges as a fundamental theorem on the stability of the equilibrium states. The new theory is not a statistical theory, it requires no layer of statistical or information-theoretic reasoning, it requires no underlying distinction between microscopic and macroscopic description, and it is not a merely phenomenological theory. It is a fundamental physical theory valid for all the systems for which quantum mechanics is usually understood to apply.

Our objective in this lecture is not to try to convince you that our new unified quantum theory is physically correct. Rather, we wish to underline that the new theory and its underlying physical hypotheses offer an entirely new perspective on the meaning of entropy, nonequilibrium, irreversibility and thermodynamics. The new perspective is indeed very unorthodox, unconventional and "revolutionary," but these are no sufficient reasons to dismiss it as "unphysical." Only a very careful scrutiny of the logical consistency and experimental verifiability of the new hypotheses could resolve the question of physical validity.

The lecture is organized as follows. First, we review the essential differences between mechanics and thermodynamics, and underline a common premise of the many proposals to rationalize such differences. Then, we propose an entirely new rationalization based on a new physical hypothesis.

MECHANICS VERSUS THERMODYNAMICS

The sciences of mechanics and thermodynamics developed quite independently and for different applications. Both sciences are physical theories of nature. Indeed, the objective of both mechanics and thermodynamics is to describe the properties of material systems and the laws governing their changes. However, the two theories give conflicting descriptions of the same physical reality. The dilemma created by such contrasts has been the subject of intensive inquiry throughout the past century.

A striking way to underline the essential distinctions between quantum mechanics and thermodynamics is to contrast their conflicting answers to the following three questions, that refer to the description of an isolated system with fixed number of particles of each type and Hamiltonian operator H with eigenvalues e_k and degeneracy D_k:

1. Among the states with given mean value $\langle H\rangle$ of the energy, how many are stable equilibrium?
2. Are there states from which it is not possible to extract all the energy (above the ground state) adiabatically, i.e., by means of a time dependent Hamiltonian $H(t)$?
3. Are irreversible processes conceivable?

The answers within quantum mechanics are:

1. None, if the given mean value $\langle H\rangle$ is not equal to one of the eigenvalues e_k. One, if $\langle H\rangle = e_k$ for some k and $D_k = 1$. Many, i.e., a (D_k-1)-fold infinity, if $\langle H\rangle = e_k$ and $D_k > 1$.
   These results follow from a straightforward analysis of the equilibrium solutions of the time-dependent Schroedinger equation $\hbar d\psi/dt = -iH\psi$, which are all stable according to Liapunoff.
2. No. By a well-known theorem proved by von Neumann,[1] for each given initial state ψ, it is always conceivable to find a time-dependent Hamiltonian $H(t)$ such that $H(0) = H$, $H(T) = H$ and the solution of the Schroedinger equation with $\psi(0) = \psi$ passes through the lowest energy ground state $\psi(T) = \varepsilon_0$ at time T, thus describing an adiabatic extraction of all the energy of the initial state in excess to the ground state energy.
3. No. By the same von Neumann theorem, given any process $\psi_1 \rightarrow \psi_2$ of the isolated system, it is always possible to find a time-dependent Hamiltonian $H(t)$ such that $H(0) = H$, $H(T) = H$ and the solution of the Schroedinger equation with $\psi(0) = \psi_2$ passes through $\psi(T) = \psi_1$ at time T, thus restoring the initial state with no net external effects. Hence, any process $\psi_1 \rightarrow \psi_2$ is reversible.

The answers within thermodynamics are:

1. One and only one, for each given value of $\langle H\rangle$. Indeed, as shown by Hatsopoulos and Keenan,[2] the statement that for each given value of the energy (and of the number of particles and the external parameters, which are fixed in our context) there exists one and only one stable equilibrium state, is a general statement of the second law of thermodynamics, which implies all the other known statements.
2. Yes. In particular, no energy can be extracted adiabatically from the stable thermodynamic equilibrium states.

3. Yes. Irreversible processes are conceivable within thermodynamics, although their existence is not required by the second law.

Mechanics and thermodynamics, therefore, seem to describe physical reality in sharply conflicting ways. This century-old dilemma is invariably resolved by stating that the true fundamental description of physical reality is given by quantum mechanics, whereas thermodynamics copes with the phenomenological description of systems whose fundamental mechanical description would be overwhelmingly complicated, hardly reproducible and, therefore, scarcely useful. Many rationalizations of the essential differences between mechanics and thermodynamics have been proposed during the past century.[3] They all share a common underlying premise, namely, that mechanics and thermodynamics occupy different levels in the hierarchy of physical theories.

A NEW HYPOTHESIS

Instead of regarding mechanics and thermodynamics as two different theories, belonging to two different levels of fundamentality, we wish to consider a new hypothesis, first conceived by Hatsopoulos and Gyftopoulos,[4] namely, that mechanics and thermodynamics are two particular aspects of a more general fundamental theory, within which the three key physical questions we just considered admit the mechanical answers for a special class of states and the thermodynamical answers in general. This can only be achieved by means of the Hatsopoulos-Gyftopoulos hypothesis that, in addition to the individual states contemplated by mechanics, there exists a new class of individual states, unconceivable within conventional mechanics, for which the mechanical answers do not necessarily apply.

We have formulated a unified quantum theory of mechanics and thermodynamics based on the new hypothesis.[5,6] We call the new theory Quantum Thermodynamics. In this lecture, we outline the main premises, postulates and theorems of the new nonstatistical theory. Quantum Thermodynamics applies to all the systems to which conventional Quantum Mechanics applies, including, for example, a single isolated two-level quantum system.

Quantum Thermodynamics contains Quantum Mechanics entirely as a special case. We present it in two stages, as is natural for any theory of nature, namely, we first postulate a kinematics, i.e., we structure the fundamental description of the individual states of a physical system, and then we postulate a dynamics, i.e., we structure the fundamental causal description of the time evolution of the individual states.

BROADER FUNDAMENTAL KINEMATICS

The quantum mechanical description of the individual states of a strictly isolated, i.e., noninteracting and uncorrelated, system with associated Hilbert space $\mathcal{H}$ is in terms of one-dimensional orthogonal projection operators P on $\mathcal{H}$. We denote by $\mathcal{P}_M$ the set of all the quantum mechanical individual states, i.e.,

$$\mathcal{P}_M = \{P \text{ on } \mathcal{H} \mid P^\dagger = P,\ P \geqq 0,\ \mathrm{Tr}P = 1,\ P^2 = P\} \tag{1}$$

Following the pioneering work of Hatsopoulos and Gyftopoulos,[4] our hypothesis is that, in addition to the quantum mechanical states in $\mathcal{P}_M$, a strictly isolated system has also access to a new class of nonmechanical individual states that must be described by self-adjoint, nonnegative-definite, unit-trace operators ρ on $\mathcal{H}$ that are not idempotent, i.e., such that $\rho^2 \neq \rho$. We denote by $\mathcal{P}$ the set of all quantum thermodynamic individual states, i.e.,

$$\mathcal{P} = \{\rho \text{ on } \mathcal{H} \mid \rho^\dagger = \rho,\ \rho \geqq 0,\ \mathrm{Tr}\rho = 1\} \tag{2}$$

Clearly, set $\mathcal{P}$ contains set $\mathcal{P}_M$ entirely. Indeed, set $\mathcal{P}_M$ contains the extreme points of convex set $\mathcal{P}$.

Operators ρ in $\mathcal{P}$ have the same defining *mathematical* properties as the von Neumann statistical or density operators of quantum statistical mechanics, but in Quantum Thermodynamics their *physical* meaning is entirely different. They do *not* represent the index of statistics from a generally heterogeneous ensemble of identical systems possibly distributed over a range of different quantum mechanical individual states. Operators ρ represent the quantum thermodynamic individual states in exactly the same sense in which state vectors ψ represent the quantum mechanical individual states. To stress this extremely important point, we call operators ρ the *state* operators.

Some physical observables are represented by linear functionals on $\mathcal{P}$. Thus, the linear functional $a(\cdot)$ associated with a physical observable A, e.g., the magnetic moment in a given direction, is given by

$$a(\cdot) = \mathrm{Tr}A\cdot \tag{3}$$

and the value of the observable for a system in individual state ρ is given by $a(\rho) = \mathrm{Tr}A\rho$. The set of all linear and nonlinear functionals on $\mathcal{P}$ represents the set of all intrinsic *state properties* of the system, because the individual state operator ρ fixes uniquely their values. As shown by Hatsopoulos and Gyftopoulos,[4] and by Ochs[7] in a more rigorous and technical mathematical framework, the only functional $s(\cdot)$ on $\mathcal{P}$ that could represent the intrinsic entropy of a strictly isolated system in every quantum thermodynamic individual state is

$$s(\rho) = -k\mathrm{Tr}\rho\ln\rho \tag{4}$$

In particular, $s(\cdot)$ is the only functional[4,7] which:

(i) is invariant under all unitary processes on $\mathcal{P}$;
(ii) is additive for independent systems; and
(iii) is equal to the same constant (zero) for all mechanical states.

NONLINEAR FUNDAMENTAL DYNAMICS

The quantum *mechanical* causal description of the time evolution of the individual states of a strictly isolated system is given by the time-dependent Schroedinger equation of motion, which in terms of the projection operators P in $\mathcal{P}_M$ becomes

$$\frac{d}{dt}P = -\frac{i}{\hbar}[H,P] \tag{5}$$

Because in Quantum Thermodynamics we postulate the existence of a broader class of individual states, we must also postulate a law of causal evolution valid in general for both the mechanical and the new nonmechanical individual states. For a single strictly isolated constituent of matter, i.e., a single particle or a single field, with Hamiltonian operator H and number operators $N_1, \ldots, N_r$ for each type of particle in the field ($[N_i,H] = 0$ for $i = 1, \ldots, r$), we postulate that the fundamental causal description of the time evolution of all the quantum thermodynamic individual states is given by the equation of motion proposed by the author,[8] i.e.,

$$\frac{d}{dt}\rho = -\frac{i}{\hbar}[H,\rho] - \frac{1}{\tau}\,\frac{1}{2}\left(\sqrt{\rho}D(\rho) + D^{\dagger}(\rho)\sqrt{\rho}\right) \tag{6}$$

where τ is an intrinsic relaxation time constant whose value can only be determined experimentally, and operator $D(\rho)$ is a nonlinear function of the state operator ρ given by

$$D(\rho) = \sqrt{\rho}\ln\rho - (\sqrt{\rho}\ln\rho)_{L(\sqrt{\rho},\sqrt{\rho}H,\sqrt{\rho}N_1,\ldots,\sqrt{\rho}N_r)} \tag{7}$$

The notation and explicit forms for $D(\rho)$ are discussed in our first lecture in this volume. The generalization of the equation of motion for systems composed of more than one constituent of matter is given in Reference 6.

For mechanical states in $\mathcal{P}_M$, i.e., for $\rho = \rho^2 = P$, Equation 6 reduces to the Schroedinger Equation 5 and, hence, Quantum Thermodynamics contains indeed the whole of Quantum Mechanics, i.e., it contains all the quantum mechanical individual states and all their unitary time evolutions. Along every solution of Equation 6, the mean values of the energy and the number of particles of each type are time invariant, and the rate of change of the entropy functional is always nonnegative. Thus, the fundamental equation of motion postulated in quantum thermodynamics for a single isolated constituent of matter entails the theorems of energy conservation, number of particle conservation and entropy nondecrease. The equation implies an explicit formula for the rate of entropy production valid for all states, close and far from equilibrium, namely, $ds(\rho)/dt = kTrD^{\dagger}(\rho)D(\rho)/\tau$. It also implies a generalization to all nonequilibrium states of Onsager's reciprocal relations and gives explicit formulae for the Onsager coefficients which emerge as nonlinear functionals of the individual state operator.[9]

The equation entails a rich variety of equilibrium solutions and unitary limit cycles. However, all the limit cycles, including all the unitary evolutions of the quantum mechanical states, and all the equilibrium solutions, with the exception of the equilibrium states with maximum entropy among the states with same mean values of the energy and the number of particles, are unstable according to Liapunoff. Very interestingly, the quantum mechanical equilibrium states (stationary states), that are all stable within Quantum Mechanics because the stability analysis is limited to the set $\mathcal{P}_M$ of mechanical states obeying the Schroedinger equation of motion, become unstable within Quantum Thermodynamics, because the stability analysis must be broadened to the set $\mathcal{P}$ of individual states obeying our general nonlinear equation of motion. For every set of mean values of the energy and the number of particles, there is one and only one stable equilibrium state. This is a statement of the second law of thermodynamics which, therefore, is entailed as a fundamental theorem of our unified quantum theory.

CONCLUSIONS

We presented a unified quantum theory of mechanics and thermodynamics new to physics. The new theory, that we call Quantum Thermodynamics, contains both Quantum Mechanics and equilibrium thermodynamics as special cases. In addition, it entails a general, definite description of nonequilibrium states and their law of relaxation towards stable equilibrium. Quantum Thermodynamics is to be understood as a new fundamental theory, playing the same role that we are used to assign to Quantum Mechanics. It is not a statistical theory, nor a merely phenomenological theory, nor an information theory. Entropy emerges as an intrinsic property of matter in the same sense as energy emerges as an intrinsic property of matter. Irreversibility emerges as an intrinsic feature of the fundamental dynamical law obeyed by the individual elementary contituents of matter. The second law emerges as a theorem of the law of causal evolution and, therefore, acquires the same level of fundamentality as the great conservation principles.

We believe that the new unified and generalized nonstatistical quantum theory is logically consistent, mathematically sound and physically appealing. The theory and, in particular, its equation of motion is definite enough to call for further careful scrutiny of its conceptual consequences, and experimentally verifiable implications. The theory does not contradict any of the successes of quantum mechanics, but contains a richer variety of physical implications. For example, it gives explicit and general formulas for the rate of entropy production and for the relaxation of individual nonmechanical nonequilibrium states towards equilibrium. Conceptually, Quantum Thermodynamics shows that the key premises of the conventional statistical rationalizations of thermodynamics, such as the key distinction between microscopic and macroscipic reality, and the key role played by heat baths and reservoirs, are not inevitable. Thus, the questions with which we started our lecture remain short of definitive answers and call for further theoretical and experimental efforts of clarification.

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