

Building on the Legacy of Professor Keenan. Entropy An Intrinsic Property of Matter

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Abstract. In the scientific and engineering literature, entropy - the distinguishing feature of thermodynamics from other branches of physics - is viewed with skepticism, and thought to be not a physical property of matter - like mass or energy - but a measure either of disorder in a system, or of lack of information about the physics of a system in a thermodynamic equilibrium state, and a plethora of expressions are proposed for its analytical representation. In this article, I present briefly two revolutionary nonstatistical expositions of thermodynamics (revolutionary in the sense of Thomas Kuhn, *The Structure of Scientific Revolutions*, U. Chicago Press, 1970) that apply to all systems (both macroscopic and microscopic, including one spin or a single particle), to all states (thermodynamic equilibrium, and not thermodynamic equilibrium), and that disclose entropy as an intrinsic property of matter.

The first theory is presented without reference to quantum mechanics even though quantum theoretic ideas are lurking behind the exposition. The second theory is a unified quantum theory of mechanics and thermodynamics without statistical probabilities, that is, I am not presenting another version of statistical quantum mechanics.

ENCOMIUM

I am deeply moved by my participation in this gathering honoring the memory of Professor Keenan. His clarity of thinking and his demand for rational conceptions about and logical conclusions of scientific and engineering efforts had a lasting influence on my academic career. The clarity and rigor of his scientific and engineering thinking inspired George N. Hatsopoulos and me to develop a nonstatistical theory of quantum thermodynamics, and Gian Paolo Beretta and me to develop a novel theory of thermodynamics. I would like to express my gratitude to Professor Keenan by translating a brief greek prayer: "light be the earth that covers him forever".

INTRODUCTION

Given that many ideas about thermodynamics were introduced in the 19th and 20th centuries, we might have assumed that there is little controversy about its foundations. However, even a cursory review of the relevant literature shows that this is not the case [1–9].

About forty years ago, a group at MIT began a response to the concerns raised about the correct foundations of the subject, which I present below not necessarily in the chronological order it was developed. Gyftopoulos and Beretta [10] have composed an exposition of thermodynamics in which all basic concepts are defined completely and

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without circular and ambiguous arguments in terms of the mechanical ideas of space, time, and force or inertial mass only. Hatsopoulos and Gyftopoulos [11] conceived a unified quantum theory of mechanics and thermodynamics, and Beretta et. al. [12, 13] discovered a complete equation of motion for the unified theory just cited. Both quantum mechanical developments involve only quantum mechanical and no statistical probabilities of the types used in either statistical classical mechanics, or statistical quantum mechanics.

In what follows, I present the foundations of thermodynamics in Sections 2 and 3, the foundations of the unified quantum theory without the equation of motion in Section 4, and conclusions in Section 5.

THERMODYNAMICS

Definition

We define *thermodynamics* as the study of motions of physical constituents resulting from externally applied forces, and from internal forces. This definition is identical to that given by Timoshenko and Young about mechanical dynamics [14]. However, because of the first and the second laws, we will see that the definition encompasses a much broader spectrum of phenomena than mechanical dynamics.

Kinematics: Conditions at an Instant in Time

We give precise definitions of the terms system, property, and state so that each definition is valid without change in any paradigm of physics, and involves no statistics.

A *system* is defined as a collection of r constituents with amounts $\mathbf{n} = \{n_1, n_2, \dots, n_r\}$ subject to s external forces or parameters $\boldsymbol{\beta} = \{\beta_1, \beta_2, \dots, \beta_r\}$. One parameter may be volume $\beta_1 = V$, and another an externally applied electric field $\beta_2 = \mathcal{E}$.

At any instant in time, each amount and each parameter have specific values.

By themselves, the values of the amounts of constituents and of the parameters do not characterize completely the condition of a system at that time. We also need the values of a complete set of linearly independent properties at the same instant in time. A *property* is defined as an attribute that can be evaluated at any instant in time by a set of measurements.

For a given system at an instant in time, the values of \mathbf{n} , $\boldsymbol{\beta}$, and of a complete set of linearly independent properties encompass all that can be said about the system at that instant. We call this complete characterization the *state* of the system, and recognize that it applies to all paradigms of physics.

Dynamics: Changes of State in Time

The state of a system may change in time either spontaneously due to the internal forces, or as a result of interactions with other systems, or both. The relation that describes the evolution of the state of either an isolated system, or of a system subject to forces that do not violate the definition of the system is the *equation of motion*. The equation of motion is discussed by Beretta in these proceedings. For the nonce, I note that many features of the complete equation of motion have been discovered, and that two of the most general and well-established features are captured by the three laws of thermodynamics discussed later.

Energy and Energy Balance

Energy is a concept that underlies our understanding of all physical phenomena. It emerges from a fundamental principle known as the first law of thermodynamics.

The *first law* asserts that any two states of a system may always be the initial and final states of a weight process, i.e., a process that involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight Mg , where M is the mass of the weight, and g the gravitational acceleration. Many other mechanical effects may be used instead of the weight for the definition of the first law.

The main consequence of this law is that every system A in state A_1 has a property called *energy*, with a value E_1 . The value of E_1 can be evaluated with respect to a reference state A_0 to which is assigned an arbitrary reference value E_0 so that

$$E_1 = E_0 - Mg(z_1 - z_0) \quad (1)$$

Energy is shown to be an *additive property* [10], that is, the energy of a composite system is the sum of the energies of the subsystems. Moreover, it is also shown that energy has the same value at the final time as at the initial time if the system experiences a zero-net-effect weight process, and remains invariant in time if the process is spontaneous. In either of the processes just cited, $z_2 = z_1$ and $E(t_2) = E(t_1)$ for time $t_2 > t_1$, that is, energy is *conserved*. Energy conservation is a time-dependent result, and is here established without use of the relevant equation of motion.

Energy is transferred between systems as a result of interactions. Denoting by $E^{A\leftarrow}$ the amount of energy transferred from the environment to system A in a process that changes the state of A from A_1 to A_2 , we can write the *energy balance*. This balance is based on the additivity and conservation of energy, and reads

$$(E_2 - E_1)_{\text{system } A} = E^{A\leftarrow} \quad (2)$$

The arrow indicates that $E^{A\leftarrow}$ is positive if energy is transferred to the system.

For most practical applications relativistic effects are negligible, and a mass balance of the form

$$(m_2 - m_1)_{\text{system } A} = m^{A\leftarrow} \quad (3)$$

is a satisfactory approximation, and $m^{A\leftarrow}$ is positive if mass is transferred to the system.

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 range of values, the number of possible states of a system is infinite. The discussion of these states is facilitated if they are classified into different categories according to evolutions in time. This classification brings forth many important aspects of physics, and provides a readily understandable motivation for the introduction of the second law of thermodynamics.

The classification consists of unsteady states, steady states, nonequilibrium states, and equilibrium states. *Unsteady* and *steady states* occur as a result of sustained (continuous) interactions of the system with its environment. A *nonequilibrium* state is one that changes spontaneously as a function of time. An *equilibrium state* is one that does not change in time while the system is isolated. An *unstable equilibrium state* is an equilibrium state that may be caused to proceed spontaneously to a sequence of entirely different states by means of a minute and short-lived interaction that has either an infinitesimal and temporary effect or a zero net effect on the state of the environment. A *stable equilibrium state* 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. These definitions are identical to the corresponding definitions in mechanics but include a much broader spectrum of states than those encountered in mechanics on account of the first and the second laws of thermodynamics.

Reversible and Irreversible Processes

A process is *reversible* if it can be performed in at least one way such that both the system and its environment are restored to their respective initial states. A process is *irreversible* if it is impossible to restore both the system and its environment to their respective initial states.

Second Law

The second law of thermodynamics is a statement of existence of stable equilibrium states. More than the first, the second law distinguishes thermodynamics from mechanics and other branches of physics.

The existence of stable equilibrium states is not self-evident. It was recognized by Hatsopoulos and Keenan [15] as the essence of the second law. Gyftopoulos and Beretta [10] concur with this recognition, and state the second law as follows: *Among all the states of a system with given values of energy, amounts of constituents, and parameters, there exists one and only one stable equilibrium state.* For each set of the conditions just cited, the stability is not local but global [16]. *Moreover, starting from any state of a system, it is always possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible*

weight process.

The existence of stable equilibrium states for the conditions specified and therefore the second law cannot be derived from the laws of mechanics. Within mechanics, the stability analysis yields that among all the allowed states of a system with fixed values of amounts of constituents and parameters, the only stable equilibrium state is that of lowest energy. In contrast, the second law avers the existence of a globally stable equilibrium state for each value of the energy. As a result, for every system the second law implies the existence of a broad class of states in addition to the states contemplated by mechanics.

The existence of stable equilibrium states for various conditions of a system has many theoretical and practical consequences. One consequence is that, starting from a stable equilibrium state of any system, no energy is available to affect a mechanical effect while the values of the amounts of constituents, the internal forces and the parameters of the system experience no net changes [10]. This consequence is often referred to as the *impossibility of the perpetual motion machine of the second kind* (PMM2). In some expositions of thermodynamics, it is taken as the statement of the second law. In this exposition, it is only a theorem of our statements of both the first and the second laws and the set of rigorous definitions that provide their rigorous framework. Moreover, it does not suffer the circularity inherent in the Kelvin-Planck statement of the second law.

Another consequence is that not all states of a system can be changed to a state of lower energy by means of a mechanical effect. This is a generalization of the impossibility of a PMM2. In essence, it is shown that a novel important property exists which is called *generalized adiabatic availability* and denoted by Ψ [10]. The generalized adiabatic availability of a system in a given state represents the optimum amount of energy that can be exchanged between the system and a weight in a weight process that begins with system A in a state A'_1 with values $\mathbf{n}'_1, \boldsymbol{\beta}'_1$, and ends in a state A'_2 with values $\mathbf{n}'_2, \boldsymbol{\beta}'_2$. Like energy, this property is well-defined for all systems and all states, but unlike energy it is not additive [10].

Reservoirs

In striving to define an additive property that captures the important features of generalized adiabatic availability, Gyftopoulos and Beretta introduce a special reference system, called a *reservoir*, and discuss the possible weight processes that the composite of a system and a reservoir R may experience. A *reservoir* is an idealized kind of system that approaches the following three limiting conditions.

1. It passes through stable equilibrium states only.
2. In the course of finite changes of state, it remains in mutual stable equilibrium with a duplicate of itself that experiences no such changes.
3. At constant values of amounts of constituents and parameters of each of two reservoirs initially in mutual stable equilibrium, energy can be transferred reversibly from one reservoir to the other with no net effects on any other system.

Two systems are in *mutual stable equilibrium* if their composite system is in a stable equilibrium state.

Available Energy

Given a reservoir R with fixed values of amounts of constituents and parameters, the adiabatic availability of the composite of system A and reservoir R is an additive property of system A called *available energy with respect to reservoir R* , and denoted by Ω_1^R .

The available energy Ω_1^R - with respect to reservoir R - of a system A in any state A_1 is the largest amount of energy that can be transferred to a weight in a weight process for the composite of system A and reservoir R without net changes in the values of the amounts of constituents and the parameters of the system and the reservoir. When Ω_1^R is transferred out, systems A and R are left in mutual stable equilibrium, that is, their composite system is in a stable equilibrium state.

The first scientist who raised the question about the largest amount of energy that can be transferred to a weight in a weight process for the composite of a system A and a reservoir R was Carnot. He restricted his investigation, however, to A also being a reservoir. His results constitute the seminal ideas - the conception event - of the science of thermodynamics. The discussion of the available energy Ω_1^R as a property is a generalization of the results of Carnot in that system A need not be a reservoir, and state A_1 need not be a stable equilibrium state. Available energy can be assigned to any system in any state.

Generalized Available Energy

Another property, the *generalized available energy* [10], may also be defined as a property of system A in any state A_1 and a reservoir R (Fig. 1). Its definition is identical to that of available energy except that the final state $A_{1'}$ of system A corresponds to arbitrarily assigned values of the amounts of constituents and parameters, that differ in general from those of state $A_{2''}$. The generalized available energy of state $A_{1'}$ is defined with respect to reservoir R and the arbitrarily assigned values of the amounts of constituents and parameters, that differ in general from those of state $A_{1'}$. For simplicity, we denote this property by the same symbol Ω_1^R as for the available energy and for the sake of simplicity disregard the prime and double prime notation. We distinguish the generalized available energy from available energy of state A_1 with respect to reservoir R by name and context.

The difference between the generalized available energies, $\Omega_1^R - \Omega_2^R$, of two states $A_{1'}$ and $A_{2''}$ is equal to the energy that can be exchanged with a weight in a reversible weight process of the composite AR of system A and reservoir R as system A goes from state $A_{1'}$ to state $A_{2''}$. Upon denoting the energy exchanged with the weight in a reversible process by $(W_{12}^{AR \rightarrow})_{\text{rev}}$, we have

$$(W_{12}^{AR \rightarrow})_{\text{rev}} = \Omega_1^R - \Omega_2^R \quad (4)$$

The value of $(W_{12}^{AR \rightarrow})_{\text{rev}}$ is positive if energy is transferred from the composite AR to the weight, and then it is the largest energy transfer to the weight that can be achieved as system A goes from state $A_{1'}$ to state $A_{2''}$. It is negative if energy is transferred from the

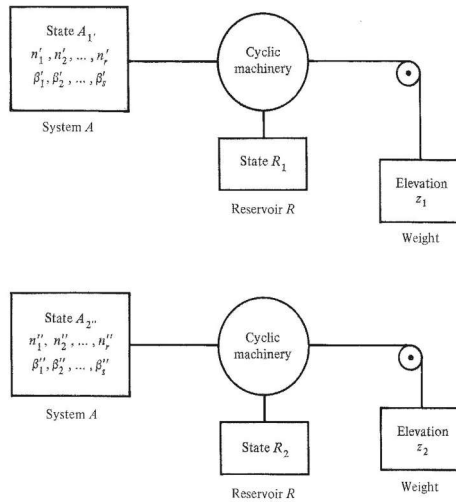


FIGURE 1. End states of weight process involved in the discussion of generalized available energy.

weight to the composite AR , and then it is the least energy transfer that is required to achieve the change of A from state A_1' to state A_2'' .

Two important relations exist between the energies E_1 and E_2 , and the generalized available energies Ω_1^R and Ω_2^R of any two states A_1' and A_2'' of system A . By virtue of the first law, the two states can always be interconnected by means of a weight process for system A alone. But the first law determines neither the direction of the weight process, nor its reversibility. By contrast, a comparison between the difference in energies and the difference in generalized available energies of the two states determines both the direction and the reversibility of the process. Specifically, if

$$\Omega_1^R - \Omega_2^R = E_1 - E_2 \quad (5)$$

then a weight process for A alone is possible both from A_1' to A_2'' and from A_2'' to A_1' , and is reversible. However, if

$$\Omega_1^R - \Omega_2^R > E_1 - E_2 \quad (6)$$

then a weight process for A alone is possible only from A_1' to A_2'' , and is irreversible.

More details about Ω^R are given in [10].

Entropy and Entropy Balance

An important consequence of the two laws of thermodynamics is that every system A in any state A_1 with energy E_1 and generalized available energy Ω_1^R with respect to auxiliary reservoir R has a property called *entropy*, denoted by the symbol S_1 . Entropy

is a property, in the same sense that energy is a property, and is defined by the relation

$$S_1 = S_0 + \frac{1}{c_R} [(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)] \quad (7)$$

where c_R is a well-defined positive constant, and A_0 is an arbitrary reference state. For a given auxiliary reservoir R , c_R is selected in such a way that the values of entropy found by means of Eq. (7) are independent of the reservoir. In other words, despite the dependence of the difference of generalized available energies $\Omega_1^R - \Omega_0^R$ in Eq. (7) on the selection of the reservoir R , we can show that there is a constant property c_R of reservoir R that makes the right hand side of Eq. (7) independent of R . Thus, S is a property of system A only. In due course, the concept of temperature is defined as a property of stable equilibrium states. Then we show that the temperature of a reservoir is constant, and that c_R is equal to the constant temperature of the reservoir.

Reversible and Irreversible Processes

Because energy and generalized available energy satisfy relations (5) and (6), the entropy defined by Eq. (7) remains invariant in any reversible adiabatic process of A , and increases in any irreversible adiabatic process of A . These conclusions are valid also for spontaneous processes, and for zero-net-effect interactions. The latter features are known as *the principle of non-decrease of entropy*. Both a spontaneous process and a zero-net-effect interaction are special cases of an adiabatic process of system A .

The entropy created as a system proceeds from one state to another during an irreversible process is called *entropy generated by irreversibility*. It is positive. The entropy non-decrease is a time-dependent result. In the novel exposition of thermodynamics [10], this result is obtained without use of the complete equation of motion. Because both energy and generalized available energy are additive, Eq. (7) implies that entropy is also additive.

Like energy, entropy can be transferred between systems by means of interactions. Denoting by $S^{A\leftarrow}$ the amount of entropy transferred from systems in the environment to system A as a result of all interactions involved in a process in which the state of A changes from state A_1 to state A_2 , we derive a very important analytical tool, the *entropy balance*, that is

$$(S_2 - S_1)_{\text{system } A} = S^{A\leftarrow} + S_{\text{irr}} \quad (8)$$

where S_{irr} is non-negative. A positive S_{irr} represents the entropy generated spontaneously within system A in the time interval from t_1 to t_2 required to affect the change from state A_1 to state A_2 . Spontaneous entropy generation within a system occurs if the system is in a state that is not stable and then the internal system dynamics precipitate the natural tendency toward stable equilibrium.

The dimensions of S depend on the dimensions of both energy and c_R . It turns out that the dimension of c_R is independent of the dimensions used in non-thermodynamic theories of physics. It is the same as the dimension of temperature. Temperature is defined below. From Eq. 7, it follows that the dimensions of S are energy over temperature.

Properties of Stable Equilibrium States

Among the many states of a system that have given values of energy E , the amounts of constituents \mathbf{n} , and parameters $\boldsymbol{\beta}$, the second law specifies that one and only one be a stable equilibrium state. It follows that any property of such a state must also be a function of E , \mathbf{n} , and $\boldsymbol{\beta}$, and that the entropy must be given by the relation

$$S = S(E, \mathbf{n}, \boldsymbol{\beta}) \quad (9)$$

Equation (9) is called the *fundamental relation*.

The fundamental relation is analytic in each of its variables, concave with respect to energy [10], that is,

$$\left[\frac{\partial^2 S}{\partial E^2} \right]_{\mathbf{n}, \boldsymbol{\beta}} \leq 0 \quad (10)$$

and is used to define other properties of stable equilibrium states, such as *temperature* T

$$\frac{1}{T} = \left[\frac{\partial S}{\partial E} \right]_{\mathbf{n}, \boldsymbol{\beta}} \quad (11)$$

total potentials

$$\mu_i = -T \left[\frac{\partial S}{\partial n_i} \right]_{E, \mathbf{n}, \boldsymbol{\beta}} \quad \text{for } i = 1, 2, \dots, r \quad (12)$$

and *pressure* p

$$p = T \left[\frac{\partial S}{\partial V} \right]_{E, \mathbf{n}, \boldsymbol{\beta}} \quad \text{for } \beta_i = V = \text{volume} \quad (13)$$

The temperature, total potentials, and pressure of a stable equilibrium state appear in the necessary conditions for systems to be in mutual stable equilibrium, that is, in states that do not affect each other. The conditions are temperature equality, total potential equalities, and pressure equality. Moreover, these equalities are the bases for the measurements of T , μ_i 's, and p .

The ranges of values of T , μ_i 's, and p are infinite. This fact can be established by careful considerations of the behavior of interactions induced by differences in temperature, total potentials, and pressure, and easily proven by quantum mechanical analyses. If quantum mechanical concepts are not used, then the ultimate values of temperature are expressed in the form of the *third law* of thermodynamics as follows. *For each given set of values of the amounts of constituents, the internal forces, and the parameters of a system without upper limit on its energy, there exists one stable equilibrium state with infinite inverse temperature, or, equivalently, zero temperature. For systems with both a lower and an upper limit on energy, such as a system consisting of a finite number of spins only, then there exist two stable equilibrium states with extreme temperatures, one with a positive inverse temperature equal to $+\infty$, and the other with a negative inverse temperature equal to $-\infty$.*

Work and Heat

A system can experience a great variety of interactions with systems in its environment. Here, we discuss only two of these interactions, work and heat.

Work is an interaction in which the system exchanges only energy with systems in its environment, without any exchange of entropy and/or constituents. If the amount of energy exchanged is W^\rightarrow , then the energy and entropy balances are

$$E_{\text{final}} - E_{\text{initial}} = \Delta E_{\text{system}} = -W^\rightarrow \quad (14)$$

$$S_{\text{final}} - S_{\text{initial}} = \Delta S_{\text{system}} = S_{\text{irr}} \quad (15)$$

where the arrow indicates that W^\rightarrow is positive if energy flows out of the system, and therefore the energy of the system decreases.

Heat is an interaction in which the system exchanges only energy and entropy with a reservoir in its environment and nothing else.¹ The amount of energy exchanged is denoted by Q^\leftarrow and the entropy by Q^\leftarrow/T_R , where T_R is the fixed temperature of the reservoir, and the arrow indicates that Q^\leftarrow is positive if energy flows into the system. It is noteworthy that Q^\leftarrow is not a function of T_R because, by definition, a reservoir has the same T_R for any value Q^\leftarrow . Thus, for a system experiencing only a heat interaction, the energy and entropy balances are

$$\Delta E_{\text{system}} = Q^\leftarrow \quad (16)$$

$$\Delta S_{\text{system}} = Q^\leftarrow/T_R + S_{\text{irr}} \quad (17)$$

In practically all expositions of thermodynamics, entropy is claimed to be defined by a relation of the form $S = \int dQ/T + S_{\text{irr}}$. To be meaningful, the temperature T in this integral must be a function of Q , but such a function is nonexistent.

Detailed discussions of properties of stable equilibrium states, such as the *fundamental relation, temperature, total potentials, and pressure*, and of different interactions, such as *work* and a more general definition of *heat* are given in Ref. [10], Chapters 8-12.

General Characteristics of the Expression of S

From the discussions in the preceding sections and our knowledge of classical thermodynamics, we conclude that any expression that purports to represent the entropy S of thermodynamics must have at least the following eight characteristics or, equivalently, conform to the following eight criteria.

1. The expression must be well-defined for every system (large or small) and every state (stable equilibrium or not stable equilibrium).
2. The expression must be invariant in all reversible adiabatic processes, and increase in any irreversible adiabatic process.

¹ Alternatively, heat can be defined as an interaction causing exchanges of energy and entropy only.

3. The expression must be additive for all well-defined systems and all states of such systems.
4. The expression must be non-negative, and vanish for all the states encountered in mechanics.
5. For given values of the energy, the amounts of constituents, and the parameters, one and only one state must correspond to the largest value of the expression.
6. For given values of the amounts of constituents and parameters, the graph of entropy versus energy of stable equilibrium states must be concave and smooth.
7. For a composite C of two subsystems A and B , the expression must be such that the entropy maximization procedure for C [criterion no. (5)] yields identical thermodynamic potentials (for example, temperature, total potentials, and pressure) for all three systems A , B , and C .
8. For stable equilibrium states, the expression must reduce to relations that have been established experimentally and that express the entropy in terms of values of energy, amounts of constituents, and parameters, such as the relations for ideal gases.

It is noteworthy that: (a) except for criteria (1) and (4), we can establish the remaining six criteria by reviewing the behavior of entropy of classical thermodynamics. These criteria are important in determining the quantum mechanical expression for entropy.

Comment

The definition of entropy introduced here differs from and is more general than the entropy presented in practically all textbooks on physics and thermodynamics. The new definition does not involve the concepts of temperature and heat; it is not restricted to large systems; it applies to macroscopic as well as microscopic systems, including a system with one spin only; it is not restricted to thermodynamic equilibrium; and it is not statistical. Despite these and other differences, for thermodynamic equilibrium states it has the same values as those listed in existing tables. It is a bona fide property of matter in the same sense that mass, velocity, energy, etc. are physical properties.

QUANTUM THERMODYNAMICS

Definition

We present a summary of a quantum theory that differs from the presentations in practically every textbook on the subject. The key differences are the recognitions that: (i) the probabilities associated with ensembles of measurement results at an instant in time require a nonstatistical density operator $\rho \geq \rho^2$, i.e., a ρ represented by a homogeneous ensemble, and (ii) the evolution in time of ρ requires an equation delimited by but more general than the Schrödinger equation [17].

Our definitions, postulates, and major theorems of quantum theory are based on slightly modified statements made by Park and Margenau [18], and close scrutiny of the implications of these statements.

In response to the first difference, Hatsopoulos and Gyftopoulos [11] observed that there exist two classes of quantum problems. In the first class, the quantum-mechanical probabilities associated with measurement results are fully described by wave functions or projectors, whereas in the second class the probabilities just cited require density operators that involve no statistical averaging over projectors - no mixtures of quantum and statistical probabilities. The same result emerges from the excellent review of the foundations of quantum mechanics by Jauch [19]. In addition, this difference eliminates the “monstrosity” of the concept of mixed state that concerned Schrödinger [20] and Park [21].

In response to the second difference, Beretta et al [12, 13] conceived a nonlinear equation of motion for nonstatistical density operators that consists of a linear part plus a nonlinear part. The equation is discussed by Beretta in these proceedings.

Kinematics: Definitions, Postulates, and Theorems at an Instant in Time

System. The term system is defined exactly the same way as in Section 2.2.

System postulate. To every system there corresponds a complex, complete, inner product space, a Hilbert space \mathcal{H} . The Hilbert space of a composite system of two distinguishable and identifiable subsystems 1 and 2, with associated Hilbert spaces \mathcal{H}^1 and \mathcal{H}^2 , respectively, is the direct product space $\mathcal{H}^1 \otimes \mathcal{H}^2$.

Homogeneous or unambiguous ensemble. At an instant in time, an ensemble of identical systems is called *homogeneous* or *unambiguous* if and only if upon subdivision into subensembles in any conceivable way that does not perturb any member, each subensemble yields in every respect measurement results - spectra of values and frequency of occurrence of each value within a spectrum - identical to the corresponding results obtained from the ensemble, Fig. 2. For example, the spectrum of energy measurement results and the frequency of occurrence of each energy measurement result obtained from any subensemble are identical to the spectrum of energy measurement results and the frequency of occurrence of each energy measurement result obtained from an independent ensemble that includes all the subensembles. Other criteria are presented in Ref. [11].

Preparation. A *preparation* is a reproducible scheme used to generate one or more homogeneous ensembles for study.

The recognition of the existence of density operators that correspond to homogeneous ensembles has many interesting applications. It extends quantum ideas to thermodynamics, and thermodynamic principles to quantum phenomena, and eliminates the need for use of statistical probabilities of statistical quantum mechanics.

Property. The term *property* refers to any attribute of a system that can be quantitatively evaluated at an instant in time by means of measurements and specified procedures. By definition, all measurement results and procedures are considered to be pre-

HOMOGENEOUS ENSEMBLE

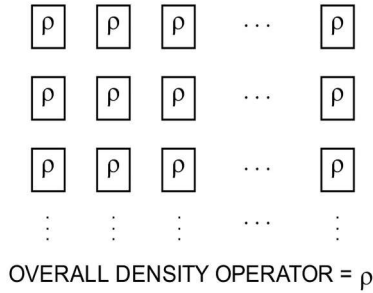


FIGURE 2. Representation of a homogeneous ensemble.

cise, that is, both error free, and unaffected by the measurement and the measurement procedures, and not to depend on either other systems or other instants in time.

Observable. From the definition just cited, it follows that each property can be observed. Traditionally, however, in quantum theory a property is called an *observable* only if it conforms to the following mathematical representation.

Correspondence postulate. Some linear Hermitian operators A, B, \dots on Hilbert space \mathcal{H} , which have complete orthonormal sets of eigenvectors, correspond to observables of a system.

The inclusion of the word “some” in the correspondence postulate is very important because it indicates that there exist Hermitian operators that do not represent observables, and properties that cannot be represented by Hermitian operators. The first category accounts for Wick et al. [22] superselection rules, and the second accounts both for compatibility of simultaneous measurements introduced by Park and Margenau [18], and for properties, such as temperature, that are not represented by operators and are defined only for restricted families of states.

Measurement act. A *measurement act* is a reproducible scheme of measurements and operations on a member of an ensemble. Regardless of whether the measurement refers to an observable or not, in principle the result of such an act is presumed to be precise, that is, an error and perturbation free number dictated solely by the system.

If a measurement act of an observable is applied to each and every member of a homogeneous ensemble, the results conform to the following postulate and theorems.

Mean-value postulate. If a measurement act of an observable represented by a Hermitian operator A is applied to each and every member of a homogeneous ensemble, there exists a linear functional $m(A)$ of A such that the value of $m(A)$ equals the arithmetic mean of the ensemble of A measurements, that is,

$$m(A) = \langle A \rangle = \sum_i a_i / N \text{ for } N \rightarrow \infty \tag{18}$$

where a_i is the result of a measurement act of A applied to the i -th member of the ensemble, a large number (theoretically infinite) of a_i 's have the same numerical value, and both $m(A)$ and $\langle A \rangle$ represent the expectation value of A .

Mean-value theorem. Each of the mean-value functionals or expectation values $m(A)$ of a system at an instant in time can also be written as

$$m(A) = \langle A \rangle = \text{Tr}[\rho A] \tag{19}$$

where ρ is an operator that is proven to be Hermitian, positive, unit trace and, in general, not a projector, that is

$$\rho > 0; \quad \text{Tr}[\rho] = 1; \quad \text{and } \rho \geq \rho^2 \tag{20}$$

The operator ρ is known as the *density operator* or the *density of measurement results of observables*, and here it can be represented solely by a homogeneous ensemble, that is, each member of the ensemble is characterized by the same ρ as any other member. It is noteworthy that the value $\langle A \rangle$ of an observable A depends exclusively on the Hermitian operator A that represents the observable and on the density operator ρ , and not on any other operator that either commutes or does not commute with operator A .

Probability theorem. If a measurement act of an observable represented by operator A is applied to each and every member of a homogeneous ensemble characterized by ρ , the probability or frequency of occurrence $W(a_n)$ that the results will yield eigenvalue a_n is given by the relation

$$W(a_n) = \text{Tr}[\rho A_n] \tag{21}$$

where A_n is the projection onto the subspace belonging to a_n

$$A|a_n^{(i)}\rangle = a_n|a_n^{(i)}\rangle \text{ for } n = 1, 2, \dots \text{ and } i = 1, 2, \dots, g_n \tag{22}$$

and g_n is the degeneracy of eigenvalue a_n .

Measurement result theorem. The only possible result of a measurement act of the observable represented by A is one of the eigenvalues of A [18].

State. The term *state* encompasses all that can be said about a system at an instant in time, that is, a set of Hermitian operators A, B, \dots that correspond to a set of $n^2 - 1$ linearly independent observables - the value of an independent observable can be varied without affecting the values of other observables - and the relations

$$\begin{aligned} \langle A \rangle &= \sum_i a_i / N \\ \langle B \rangle &= \sum_i b_i / N \\ &\dots \end{aligned} \tag{23}$$

where n is the dimensionality of the Hilbert space, and in principle $N \rightarrow \infty$. It is noteworthy that the operators A, B, \dots are determined by the system, and either the expectation values or the density operator and A, B, \dots specify the state. For a given system, the mappings both from ρ to expectation values and from expectation values to ρ are unique because Eqs. 23 are linear from expectation values to and from ρ to expectation values, where $\rho \geq \rho^2$.

It is noteworthy, that no quantum-theoretic requirement exists which excludes the possibility that the mapping from the measurable expectation values to ρ must yield a projector $\rho = \rho^2$ rather than a density operator $\rho > \rho^2$, and, conversely, that a pre-specified operator ρ must necessarily be a projector. In fact, the existence of density

operators that are not derived as a mixture of quantum probabilities and statistical probabilities provides the means for the unification of quantum theory and thermodynamics without resorting to statistical considerations [11].

Collapse of the wave function postulate. Among the postulates of quantum mechanics, many authoritative textbooks include von Neumann's projection or collapse of the wave function postulate [23, 24]. An excellent, rigorous, and complete discussion of the falsity of the projection postulate is given by Park [25].

Quantum expression for entropy. Ever since the enunciation of the first and second laws of thermodynamics by Clausius about 140 years ago, all expressions for entropy that are not based on temperature and heat involve statistical probabilities. As we discuss earlier, entropy is proven to be an intrinsic - inherent - nonstatistical property of any system in any state. Gyftopoulos and Çubukçu [26] considered all the conditions that must be satisfied by the entropy analytical expression, and show that the only function that is consistent with all conditions is

$$S = -k_B \text{Tr}[\rho \ln \rho] \quad (24)$$

CONCLUDING REMARKS

Many people believe that thermodynamics is not a fundamental theory of physics because the concept of entropy - the concept that distinguishes thermodynamics from other branches of physics - is a statistical and accurate tool for understanding phenomena associated with very large systems in a thermodynamic - chaotic - equilibrium state. I hope the preceding discussions will be helpful in changing this belief.

Some novel results are:

Maxwell's demon cannot accomplish his task because in a system in a stable equilibrium state nothing moves, the velocity of each particle is zero. So, there are no fast and slow particles to be sorted out [27].

Alternatively, for a system without upper limit on energy, Maxwell's demon cannot accomplish the task because he is asked to extract only energy from a system in a stable equilibrium state at no cost of any kind. But starting from a stable equilibrium state there exist no states of lower energy and the same entropy. Alternatively, at no cost he is asked to reduce the entropy of the gas he is manipulating but entropy is a nondestructible property of matter [28].

An interesting exception to these remarks is a spin system in the region of negative temperatures. In that region, the demon can accomplish his assignment, i.e., extract energy only from a stable equilibrium state.

Brownian movement does not represent motions. It is the result of reallocations of the constituents of a solvent and a colloid to continuously evolving energy eigenstates and eigenvalues due to shape changes of the constant volumes of the solvent and the colloid. The volume shape changes are due to infinite differences of chemical potentials between the constituents of the solvent and the colloid, and of the constituents of the colloid and the solvent [29].

The biography of e.Coli does not represent Brownian movement because the ambient and e.Coli experience chemical reactions [29].

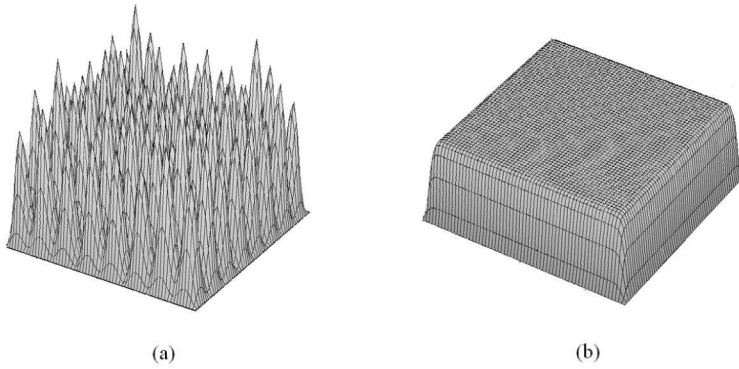


FIGURE 3. Probability density function versus position of a particle in a square box (infinitely deep potential well): (a) an equilibrium state of energy E ; and (b) stable equilibrium state of energy E . Arbitrary dimensionless units.

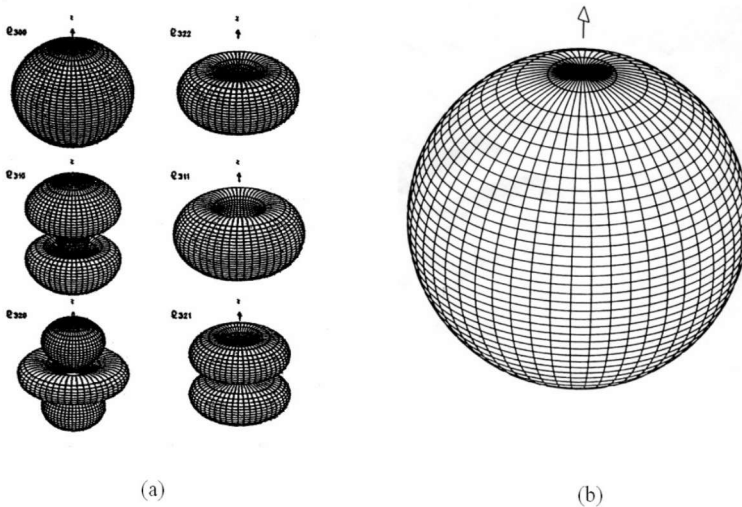


FIGURE 4. Probability density functions versus position of the electron of a hydrogen atom: (a) heterogeneous subensemble surfaces of the constant density function [31]; and (b) homogeneous ensemble surface of the electron in a stable equilibrium state (arbitrary units) [32].

Entropy is a measure of the spatial shape of the quantum probabilities associated with a state [30]. For example, for one particle with specified energy confined in a two-dimensional box, the probability distributions are oscillatory for states that are not stable equilibrium as shown in Fig. 3a. For the unique stable equilibrium state for any specified energy, the distribution is flat throughout the box except near the walls where it smoothly reduces to zero as shown in Fig. 3b. The flat or even distribution is what renders the entropy of that state larger than that of the states that correspond to the same energy but are not stable equilibrium.

Another illustration of the spatial shape of the quantum probabilities and entropy is provided by the electron of a hydrogen atom in Figs. 4a and 4b.

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