ARTICLES

Entropy: Thermodynamic definition and quantum expression

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Numerous expressions exist in the scientific literature purporting to represent entropy. Are they all acceptable? To answer this question, we review the thermodynamic definition of entropy, and establish eight criteria that must be satisfied by it. The definition and criteria are obtained by using solely the general, nonstatistical statements of the first and second laws presented in *Thermodynamics: Foundations and Applications* [Elias P. Gyftopoulos and Gian Paolo Beretta (Macmillan, New York, 1991)]. We apply the eight criteria to each of the entropy expressions proposed in the literature and find that only the relation $S = -k\,\mathrm{Tr}\rho\ln\rho$ satisfies all the criteria, provided that the density operator ρ corresponds to a homogeneous ensemble of identical systems, identically prepared. Homogeneous ensemble means that every member of the ensemble is described by the same density operator ρ as any other member, that is, the ensemble is not a statistical mixture of projectors (wave functions). [S1063-651X(97)00904-5]

INTRODUCTION

In his extensive and authoritative review, Wehrl [2] writes ''It is paradoxical that although entropy is one of the most important quantities of physics, its main properties are rarely listed in the usual textbooks on statistical mechanics.'' We concur fully with this assessment, and add that the main characteristics of entropy are rarely listed even in the textbooks on thermodynamics, despite the fact that entropy is clearly a thermodynamic (not mechanical) concept.

The lack of specificity has resulted in a plethora of expressions purporting to represent the entropy of thermodynamics, and perhaps influenced von Neumann [3] to respond to Shannon's question ''What should I call $-\Sigma_i p_i \ln p_i$?'' by saying ''You should call it 'entropy' for two reasons: first, the function is already in use in thermodynamics under that name; second, and more importantly, most people don't know what entropy really is, and if you use the word entropy you will win every time!''

The purposes of this paper are to redress the omissions, and to prove that, of all the known expressions, the only one that represents entropy as a well-defined property of matter is the quantum-theoretic functional $S = -k\,\mathrm{Tr}\rho\ln\rho$. Even though the functional is very well known and more often than not rejected in statistical quantum mechanics, here the proof is solely thermodynamic, and ρ is a density operator that experimentally (in contrast to algebraically) cannot be decomposed into a statistical mixture of projectors.

The paper is organized as follows. In the second section we introduce the first and second laws of thermodynamics, and derive from them the concepts of energy and generalized available energy as properties of any system (large or small) in any state (thermodynamic equilibrium or not thermodynamic equilibrium). In the third section, we present a general thermodynamic definition of entropy in terms of energy and generalized available energy, and discuss its features. In the fourth section we list eight characteristics of this entropy which are theorems derived from the laws of thermodynamics, and which can be used as criteria of acceptance of any analytic expression purporting to represent entropy. In the fifth section we discuss briefly a recent quantum-theoretic interpretation of thermodynamics, summarize a number of quantum expressions for entropy that have appeared in the literature, and investigate whether one or more of these expressions conform with the eight criteria listed in the preceding section.

As a result of this investigation, we prove that among the candidates only the expression $S = -k\,\mathrm{Tr}\rho\ln\rho$ conforms with all the criteria, provided that the density operator ρ represents the quantum-theoretic probabilities derivable from a homogeneous ensemble of identical systems, identically prepared.

The homogeneous ensemble is a generalization of the concept introduced by von Neumann [4]. It is an ensemble of identical members in which each member is described by the same density operator ρ ($\rho \geqslant \rho^2$) as any other member, that is, the ensemble is not a statistical mixture of projectors (wave functions). In other words, experimentally as opposed to algebraically, the density operator compatible with the exposition of thermodynamics in Ref. [1] is not a mixture of quantum probabilities derived from projectors and classical statistical probabilities introduced because of either ignorance or lack of interest in the details of the system, or both, but the seat of quantum-theoretic probabilities only.

THERMODYNAMICS

General remarks

Many scientists and engineers have expressed concerns about the completeness and clarity of the usual expositions of thermodynamics. For example, in the preface of his book *Concepts of Thermodynamics*, Obert writes [5] ''Most teach-

ers will agree that the subject of engineering thermodynamics is confusing to the student despite the simplicity of the usual undergraduate presentation.'' Again, Tisza states [6] ''The motivation for choosing a point of departure for a derivation is evidently subject to more ambiguity than the technicalities of the derivation . . . . In contrast to errors in experimental and mathematical techniques, awkward and incorrect points of departure have a chance to survive for a long time.''

In response to numerous such concerns, Gyftopoulos and Beretta [1] have composed an exposition in which all basic concepts of thermodynamics are defined completely and without circular arguments in terms of the mechanical ideas of space, time, and force or inertial mass only.

The order of introduction of concepts and principles is system (types and amounts of constituents, forces between constituents, and external forces or parameters); properties; states; the first law; energy (without work and heat); energy balance; classification of states in terms of time evolutions; stable equilibrium states; second law (without temperature, heat, and entropy); generalized available energy; entropy of any state, stable equilibrium or not, in terms of energy and generalized available energy and not in terms of temperature and heat; entropy balance; fundamental relation for stable equilibrium states only; temperature, total potentials, and pressure in terms of energy, entropy, amounts of constituents and parameters for stable equilibrium states only; the third law; work in terms of energy; and heat in terms of energy, entropy, and temperature.

All concepts and principles are valid for all systems (macroscopic or microscopic), and all states (thermodynamic or stable equilibrium states, and states that are not stable equilibrium).

Definition

We define general thermodynamics or simply thermodynamics as the study of motions of physical constituents (particles and radiations) resulting from externally applied forces, and from internal forces (the actions and reactions between constituents). This definition is identical to that given by Timoshenko and Young about mechanical dynamics [7]. However, because of the second law, we will see that the definition encompasses a much broader spectrum of phenomena than mechanical dynamics.

Kinematics: conditions at an instant in time

In kinematics we give verbal definitions of the terms system, property, and state so that each definition is valid without change in any physical theory, and involves no statistics attributable to lack of information. The definitions include innovations. To the best of our knowledge, they violate no theoretical principle and no experimental result.

A *system* is defined as a collection of *constituents* subject to *internal forces*, that is, forces between constituents, and *external forces*.

Everything that is not included in the system is the *environment*.

For a system with r constituents, we denote their amounts by the vector $\mathbf{n}=\{n_1, n_2, \ldots, n_r\}$. For a system subject to external forces described by s parameters we denote the parameters by the vector $\boldsymbol{\beta}=\{\beta_1, \beta_2, \ldots, \beta_s\}$. One parameter may be volume, $\beta_1 = V$, another may be an externally determined electric field, β_2 equal to electric field.

At any instant in time, the amount of each constituent and the parameters of each external force have specific values. We denote these values by $\mathbf{n}$ and $\boldsymbol{\beta}$ with or without additional subscripts.

By themselves, the values of the amounts of constituents and of the parameters at an instant in time do not suffice to characterize completely the condition of the system at that time. We also need the values of all the properties at the same instant in time. A *property* is defined as an attribute that can be evaluated at any given instant in time (not as an average over time) by means of a set of measurements and operations that are performed on the system and result in a numerical value—the *value of the property*. This value is independent of the measuring devices, other systems in the environment, and other instants in time.

For a given system, the instantaneous 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 about the system at a given instant in time and about the results of any measurements that may be performed on the system at that same instant in time. We call this complete characterization of the system at an instant in time the *state* of the system. This definition of state, without change, applies to any branch 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 an isolated system—*spontaneous changes of state*—as a function of time is the *equation of motion*. Certain time evolutions obey *Newton's equation*, which relates the total force F on each system particle to its mass m and acceleration a so that $F = ma$. Other evolutions obey the *time-dependent Schrödinger equation*, that is, the quantum-mechanical equivalent of Newton's equation. Other experimentally observed time evolutions, however, do not obey either of these equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion that describes all physical phenomena remains a subject of research at the frontier of science—one of the most intriguing and challenging problems in physics [8].

Many features of the complete equation of motion have already been discovered. These features provide not only guidance for the discovery of the complete equation but also a powerful alternative procedure for analyses of many time-dependent, practical problems. Two of the most general and well-established features are captured by the consequences of the first and second laws of thermodynamics discussed later.

Energy and energy balance

Energy is a concept that underlies our understanding of all physical phenomena, yet its meaning is subtle and difficult to grasp. 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. Such a process involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight, that is, solely a mechanical effect. Moreover, for a given weight, the value of the expression $Mg(z_1-z_2)$ is fixed only by the end states of the system, where M is the mass of the weight, and g the gravitational acceleration.

The main consequence of this law is that every system A in any state A_1 has a property called *energy*, with a value denoted by the symbol E_1 (Ref. [1], Sec. 3.4, pp. 32 and 33). The energy E_1 can be evaluated by a weight process that connects A_1 and a reference state A_0 to which is assigned an arbitrary reference value E_0 so that

$$E_1 = E_0 - Mg(z_1 - z_0). \tag{1}$$

Energy is shown to be an additive property (Ref. [1], Sec. 3.6, pp. 34 and 35), that is, the energy of a composite system is the sum of the energies of its 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 that energy remains invariant in time if the process is spontaneous (Ref. [1], Sec. 3.7, pp. 35–37). In either of the last two processes, $z_2 = z_1$ and $E(t_2) = E(t_1)$ for time t_2 greater than t_1, that is, energy is *conserved*. Energy conservation is a time-dependent result. In Ref. [1], this result is obtained without use of the complete equation of motion.

Energy can be transferred between systems by means 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 derive the *energy balance*. This derivation is based on the additivity of energy and energy conservation (Ref. [1], Sec. 3.8, pp. 37 and 38), and reads

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

In words, the energy change of a system must be accounted for by the energy transferred across the boundary of the system.

Types of states

Because the number of independent properties of a system is infinite even for a system consisting of a single particle with a single translational degree of freedom—a single variable that fixes the configuration of the system in space—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 time evolutions. 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 (Ref. [1], Sec. 4.1, pp. 53–58). An *equilibrium state* is one that does not change as a function of time while the system is isolated—a state that does not change spontaneously. 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 only an infinitesimal 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. The broader spectrum is due to the second law discussed later.

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, experience shows that a system can transfer energy out and affect a mechanical effect without leaving any other net changes in the state of the environment. In contrast, starting from a stable equilibrium state, experience shows that a system cannot affect the mechanical effect just cited. This impossibility is one of the most striking consequences of the first and second laws of thermodynamics.

Generalized available energy

The existence of stable equilibrium states is not self-evident. It was recognized by Hatsopoulos and Keenan [16] as the essence of all correct statements of the second law. Gyftopoulos and Beretta (Ref. [1], Chap. 4, pp. 53–66) concur with this recognition, and state the *second law* as follows (simplified version): Among all the states of a system with a given value of energy, and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state.

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 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 matter 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 and parameters of the system experience no net changes (Ref. [1], Sec. 4.5, pp. 64 and 65). 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 one aspect of both the first and the second laws.

Another consequence is that not all states of a system can be changed to a state of lowest 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 (Ref. [1], Sec. 5.5, pp. 77–80). 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. Like energy, this property is well defined for all systems and all states, but unlike energy it is not additive (Ref. [1], Sec. 5.3.8, p. 75).

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 the reservoir may experience. Thus they disclose a third consequence of the first and second laws, that is, a limit on the optimum amount of energy that can be exchanged between a weight and a composite of a system and a reservoir R—the optimum mechanical effect. They call the optimum value *generalized available energy* (Ref. [1], Sec. 6.8, pp. 95–97), denote it by Ω^R, and show that it is additive (Ref. [1], Sec. 6.9.6, pp. 98 and 99). It is a generalization of the concept of motive power of fire introduced by Carnot. It is a generalization because he assumed that both systems of the composite acted as reservoirs with fixed values of their respective amounts of constituents and parameters, whereas Gyftopoulos and Beretta do not use this assumption. The definition of a reservoir is given in Ref. [1], Sec. 6.3, pp. 87 and 88.

For an *adiabatic process* (Ref. [1], Sec. 12.1, pp. 168–173) of system A only, it is shown that the energy change $E_1 - E_2$ of A and the generalized available energy change $\Omega_1^R - \Omega_2^R$ of the composite of A and reservoir R satisfy the following relations (Ref. [1], Sec. 6.9, pp. 97–99). If the adiabatic process of A is reversible,

$$E_1 - E_2 = \Omega_1^R - \Omega_2^R. \tag{3}$$

If the adiabatic process of A is irreversible,

$$E_1 - E_2 < \Omega_1^R - \Omega_2^R. \tag{4}$$

A process is *reversible* if both the system and its environment can be restored to their respective initial states. A process is *irreversible* if the restoration just cited is impossible.

It is noteworthy that energy and generalized available energy are defined for any state of any system, regardless of whether the state is steady, unsteady, equilibrium, nonequilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether the size of the system is large or small.

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 heat, are given in Ref. [1], Chaps. 8–12.

ENTROPY

Definition

A system A in any state A_1 has many properties. Two of these properties are energy E_1 and generalized available energy Ω_1^R with respect to a given auxiliary reservoir R. These two properties determine a third property called *entropy*, denoted by the symbol S. It is a property in the same sense that energy is a property, or momentum is a property. For a state A_1, S_1 can be evaluated by means of an auxiliary reservoir

R, a reference state A_0, with energy E_0 and generalized available energy Ω_0^R, to which is assigned a reference value S_0, and the expression

$$S_1 = S_0 + \frac{1}{c_R}[(E_1 - E_0) - (\Omega_1^R - \Omega_0^R)], \tag{5}$$

where c_R is a well-defined positive constant that depends on the auxiliary reservoir R only. Entropy S is shown to be independent of the reservoir (Ref. [1], Sec. 7.4, pp. 108–112), that is, S is a property of system A and the reservoir is auxiliary and is used only because it facilitates the definition of S. It is also shown that S can be assigned absolute values that are non-negative, and that vanish for all the states encountered in mechanics (Ref. [1], Sec. 9.8, pp. 137 and 138).

Because energy and generalized available energy satisfy relations (3) and (4), the entropy defined by Eq. (5) 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 nondecrease 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 nondecrease is a time-dependent result. In the exposition of thermodynamics in Ref. [1], this result is obtained without use of the complete equation of motion.

Because both energy and generalized available energy are additive, Eq. (5) implies that entropy is also additive (Ref. [1], Sec. 7.2.2, pp. 103 and 104).

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 A_1 to A_2, we derive a very important analytical tool, the *entropy balance* (Ref. [1], Sec. 7.3, pp. 106–108), that is,

$$(S_2 - S_1)_{\text{system } A} = S^{A\leftarrow} + S_{\text{irr}}, \tag{6}$$

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 nonequilibrium state in which the internal system dynamics precipitate the natural tendency towards stable equilibrium.

The dimensions of S depend on the dimensions of both energy and c_R. It turns out that the dimensions of c_R are independent of mechanical dimensions, and are the same as those of temperature (Ref. [1], Sec. 9.7, pp. 136 and 137). Temperature is defined later.

Stable equilibrium states

It is shown that among the many states of a system that have given values of the energy E, the amounts of constituents $\mathbf{n}$, and the parameters $\boldsymbol{\beta}$, the entropy of the unique stable equilibrium state that corresponds to these values is larger

than that of any other state with the same values E, $\mathbf{n}$, and $\boldsymbol{\beta}$ (Ref. [1], Sec. 8.2, pp. 119 and 120), and can be expressed as a function

$$S = S(E, \mathbf{n}, \boldsymbol{\beta}). \tag{7}$$

Equation (7) is called the *fundamental relation* (Ref. [1], Sec. 8.3, pp. 120–124).

The fundamental relation is analytic in each of its variables E, $\mathbf{n}$, and $\boldsymbol{\beta}$ (Ref. [1], Sec. 8.3, pp. 120–124), and concave with respect to energy (Ref. [1], Sec. 9.4, pp. 131 and 132), that is,

$$\left[\frac{\partial^2 S}{\partial E^2} \right]_{n,\beta} \leq 0. \tag{8}$$

Moreover, the fundamental relation is used to define other properties of stable equilibrium states, such as *temperature T* (Ref. [1], Chap. 9, pp. 127–142),

$$\frac{1}{T} = \left[\frac{\partial S}{\partial E} \right]_{n,\beta}, \tag{9}$$

total potentials μ_i for $i = 1,2, \ldots, r$ (Ref. [1], Chap. 10, pp. 147–151),

$$\mu_i = -T \left[\frac{\partial S}{\partial n_i} \right]_{E,n,\beta} \qquad \text{for} \quad i = 1,2, \ldots, r, \tag{10}$$

and *pressure p* (Ref. [1], Chap. 11, pp. 157–162),

$$p = T \left[\frac{\partial S}{\partial V} \right]_{E,n,\beta} \qquad \text{for} \quad \beta_1 = V = (\text{volume}). \tag{11}$$

The temperature, total potentials, and pressure of a stable equilibrium state appear in the necessary conditions for systems to be in mutual stable equilibrium, such as the temperature equality (Ref. [1], Sec. 9.2, pp. 129 and 130), the total potential equality (Ref. [1], Sec. 10.2, pp. 149 and 150), and the pressure equality (Ref. [1], Sec. 11.2, pp. 157–159). Moreover, these equalities are the bases for the measurements of T, μ_i's, and p.

Comment

The concept of entropy introduced here differs from and is more general than that of many textbooks. It 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, or a system with one particle with only one (translational) degree of freedom; it is not restricted to stable (thermodynamic) equilibrium states; it is defined for both stable equilibrium (thermodynamic equilibrium) and not stable equilibrium states because energy and generalized available energy are defined for all states; and most certainly, it is not statistical—it is a property of matter. These assertions are valid because here the postulates or laws of thermodynamics from which the concept of entropy originates do not involve the concepts of temperature and heat, are not restricted either to large systems or to stable equilibrium states or both, and are not statistical. To emphasize the difference and generality

of the concept, we recall contrary statements by Meixner [17]: ''A careful study of the thermodynamics of electrical networks has given considerable insight into these problems and also produced a very interesting result: the nonexistence of a unique entropy value in a state which is obtained during an irreversible process, . . . , I would say I have done away with entropy''; and Callen [18]: ''it must be stressed that we postulate the existence of the entropy only for equilibrium states and that our postulate makes no reference whatsoever to nonequilibrium states.''

CHARACTERISTICS OF ENTROPY

From the discussions in the preceding section and our knowledge of classical thermodynamics, we conclude that any expression that purports to represent the entropy 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.

(3) The expression must be additive for all systems and all states.

(4) The expression must be non-negative, and vanish for all the states encountered in mechanics.

(5) For given values of energy, amounts of constituents, and 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, chemical 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 the values of energy, amounts of constituents, and parameters, such as the relations for ideal gases.

It is noteworthy that, except for criteria (1) and (4), we can establish the remaining six criteria by reviewing the definition of entropy of classical thermodynamics.

QUANTUM EXPRESSIONS FOR ENTROPY

Ever since the enunciation of the first and second laws of thermodynamics by Clausius about 130 years ago, all expressions for entropy that are not based on temperature and heat involve probabilities. Invariably, the probabilities are statistical (as opposed to inherent to the nature of physical phenomena), and are introduced as a means to partially overcome the enormous computational and informational difficulties resulting from the complexity of the ''actual

state'' (classical or quantum) of a large system. Thus each expression of entropy is usually construed as a subjective measure of information rather than an analytical description of an objective property of matter.

Over the past two decades, a different point of view has been developed consistent with the idea that entropy is a property of matter. Hatsopoulos and Gyftopoulos [9] observed that the von Neumann concept of a homogeneous ensemble of identical systems that represents a density operator ρ equal to a projector (every member of the ensemble is described by the same projector, $\rho = \rho^2$, or the same wave function as any other member) can be readily extended to density operators that are not projectors (every member of the ensemble is described by the same density operator, $\rho > \rho^2$, as any other member, that is, the ensemble is not a statistical mixture of projectors). This extension is accomplished without any changes of the quantum-theoretic postulates about observables, measurement results, and values of observables. An identical conclusion is reached by other scientists [19].

One benefit of the observation just cited is the elimination of the monstrosity of the concept of mixed state that concerned Schrödinger [20] and Park [21].

Another even more important benefit is that the extension results in a unified quantum theory which encompasses within a single structure of concepts and mathematical representatives both mechanics and thermodynamics without any need for statistical (subjective or informational) probabilities [10]. The unified theory applies to all systems, small or large, including a one spin system, and all states, unsteady, steady, nonequilibrium, equilibrium, and stable (thermodynamic) equilibrium.

Next, Hatsopoulos and Gyftopoulos postulated that the special class of unitary transformations of ρ with respect to time obey the von Neumann equation of motion

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho] \qquad (12)$$

for both isolated systems (Hamiltonian operators H independent of time) and nonisolated systems (Hamiltonian operators H explicitly dependent on time). It is noteworthy that Eq. (12) must be introduced as a postulate because, experimentally as opposed to algebraically, a ρ that represents a homogeneous ensemble cannot be construed as a statistical mixture of projectors and therefore Eq. (12) cannot be derived from the Schrödinger equation.

As is well known, the processes described by Eq. (12) are reversible adiabatic. However, neither do all reversible adiabatic processes correspond to unitary transformations of ρ with respect to time, nor are all adiabatic processes reversible. Accordingly, as an equation of motion of physics, Eq. (12) is incomplete [8]. Its completion is one of the most challenging outstanding problems of contemporary physics.

If there exist constants of the motions of all the reversible adiabatic processes described by Eq. (12), Hatsopoulos and Gyftopoulos [10] concluded that each such constant must be a functional solely of the eigenvalues of ρ because these are the only quantities that remain invariant in the course of all unitary transformations with respect to time.

TABLE I. Criteria satisfied and not satisfied by known expressions for entropy.

Entropy expression	Criterion							
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
S_D	Y	Y	N					
S_H	Y	Y	Y	Y	N			
S_∞	Y	Y	Y	Y	Y	N		
S_R	Y	Y	Y	Y	Y	Y	N	
S_v	Y	Y	Y	Y	Y	Y	Y	Y

In the light of this point of view, and the eight criteria of the preceding section, we conclude that (a) expressions for entropy based on temperature and heat are not acceptable because they are restricted to thermodynamic or stable equilibrium states only; (b) expressions for entropy proposed in statistical classical mechanics are not acceptable because they are based on statistical (subjective) rather than quantal (inherent) probabilities, and the resulting entropy is not a property of matter; and (c) expressions for entropy proposed in statistical quantum mechanics [22,23] that depend on variables other than the eigenvalues of ρ are not acceptable because they fail criterion (2) for processes in which the changes of ρ are unitary. Accordingly, some quantum functionals that are proposed in the literature and that are candidates as possible expressions for entropy are the following.

The Daróczy entropy [24]

$$S_D = \frac{1}{2^{1-\alpha} - 1}(\mathrm{Tr}\rho^\alpha - 1), \qquad (13)$$

where $\alpha > 0$, $\alpha \neq 1$.

The Hartley entropy [25]

$$S_H = k \ln N(\rho), \qquad (14)$$

where $N(\rho)$ is the number of positive eigenvalues of ρ.

The infinite norm entropy

$$S_\infty = -k \ln \|\rho\|_\infty, \qquad (15)$$

where $\|\rho\|_\infty = p_{\text{largest}} = $ (the largest eigenvalue of ρ).

The Rényi entropy [26]

$$S_R = \frac{k}{1-\alpha} \ln(\mathrm{Tr}\rho^\alpha), \qquad (16)$$

where $\alpha > 0$, $\alpha \neq 1$.

The von Neumann entropy [27]

$$S_v = -k \, \mathrm{Tr}\rho \ln\rho. \qquad (17)$$

Applying criteria (1)–(8) of the preceding section to expressions (13)–(17), we find the results listed in Table I.

Specifically, the Daróczy entropy satisfies criteria (1) and (2) but fails criterion (3)—it is not additive [28]. Accordingly, S_D is not acceptable as an expression for entropy.

The Hartley entropy satisfies criteria (1)–(4) but fails criterion (5). For given values of energy E, amounts of constituents $\mathbf{n}$, and parameters $\boldsymbol{\beta}$, many different density opera-

tors have the same number of positive eigenvalues as the density operator that corresponds to the unique stable equilibrium state associated with E, $\mathbf{n}$, and $\boldsymbol{\beta}$. Accordingly, many states have the same value of the Hartley entropy instead of only one having the value given by the fundamental relation [Eq. (7)]. It follows that the Hartley entropy is not acceptable.

It can be easily verified that the infinite norm entropy conforms to criteria (1)–(5). To probe criterion (6), we consider a system that has only two energy eigenvalues, $-\varepsilon$ and $+\varepsilon$ (spin system). For this system and a given value of the energy E, we can write the matrix of the density operator ρ in the energy representation in the form

$$[\rho]_\varepsilon = \begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix}_\varepsilon, \qquad (18)$$

where $0 \le x \le 1$, δ is a complex number such that $|\delta|^2 \le x - x^2$, δ^* is the complex conjugate of δ, and subscript ε denotes the energy representation. The eigenvalues p_1 and p_2 of ρ satisfy the relations

$$p_1 + p_2 = 1, \quad p_1 p_2 = \mathrm{Det}(\rho) = |\rho| = x - x^2 - |\delta|^2, \quad (19)$$

that is, they are solutions of the quadratic equation

$$p^2 - p + |\rho| = 0. \qquad (20)$$

The largest eigenvalue is given by the relation

$$p_\nearrow = \tfrac{1}{2}\left(1 \pm \sqrt{1 - 4|\rho|}\right) \qquad (21)$$

and is a maximum if $|\rho|$ is a minimum, that is, if $|\delta|^2 = 0$ and

$$p_{\max} = \begin{cases} x & \text{if } x \ge \tfrac{1}{2} \\ 1-x & \text{if } x < \tfrac{1}{2}. \end{cases} \qquad (22)$$

For $|\delta|^2 = 0$ and a given value E, the density operator is diagonal in the energy representation, and represents the only equilibrium operator of the spin system.

On the other hand, the energy of the system satisfies the relation

$$E = \mathrm{Tr}(\rho H)_\varepsilon = \mathrm{Tr}\begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix}\begin{bmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{bmatrix} = \varepsilon(1-2x) \qquad (23)$$

and therefore

$$p_{\max} = \begin{cases} \dfrac{1}{2}\left[1 - \dfrac{E}{\varepsilon}\right] & \text{if } \varepsilon \le E \le 0 \\[2mm] \dfrac{1}{2}\left[1 + \dfrac{E}{\varepsilon}\right] & \text{if } 0 < E \le \varepsilon. \end{cases} \qquad (24)$$

Thus the graph of $S_\infty = -k \ln p_{\max}$ versus E is neither smooth nor concave because it has a cusp at $\varepsilon = 0$ and $d^2 S/dE^2$ is positive and not negative as required by relation (8). Accordingly, the infinite norm entropy is not acceptable.

Next, it can be shown that the Rényi entropy satisfies criteria (1)–(6) but fails criterion (7) [28]. So the Rényi entropy is not acceptable.

The von Neumann entropy satisfies all the criteria (1)–(8). So, it is the only known quantum expression of entropy that is acceptable.

Because the von Neumann entropy appears in practically every textbook on statistical quantum mechanics, some additional remarks are necessary here. In statistical quantum mechanics, several different derivations of S_v are given [22,28–30]. Each of these derivations, however, introduces hypotheses or axioms which are not consistent with the idea that entropy is a property of matter. For example, von Neumann's derivation [22,27] is based on the premise of mixing pure states (projectors). Such a premise leads to contradictions [9,11]. Again, Ochs's derivation [28] is based on the assumptions that the expression for entropy must satisfy the conditions of ''partial isometric invariance'' and ''subadditivity,'' conditions which are not justified by the laws of thermodynamics.

For a ρ that corresponds to a homogeneous ensemble, the first proof that S_v is the quantum expression for entropy is given by Hatsopoulos and Gyftopoulos [10]. However, certain features of their derivation are mathematically faulty. So, the conclusion that S_v is the only known quantum expression for entropy is the result presented here.

CLOSING REMARK

In addition to shedding some light on the meaning of entropy as a property of matter, density operators that satisfy the relation $\rho \ge \rho^2$, and that cannot be decomposed experimentally (as opposed to algebraically) into mixtures of pure states open several interesting questions at the frontier of contemporary physics. Both from the theoretical and the engineering points of view, the most important of these questions relates to the form of the complete equation of motion, the equation that applies to all processes, reversible and irreversible.

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