Thermodynamic Definition and Quantum-Theoretic Pictorial Illustration of Entropy

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Carnot analyzed an engine operating between two reservoirs. Through a peculiar mode of reasoning, he found the correct optimum shaft work done during a cyclic change of state of the engine. Clausius justified Carnot's result by enunciating two laws of thermodynamics, and introducing the concept of entropy as a ratio of heat and temperature of a thermodynamic equilibrium state. In this paper, we accomplish five purposes: (i) We consider a Carnot engine. By appropriate algebraic manipulations we express Carnot's optimum shaft work in terms of available energies or exergies of the end states of one reservoir with respect to the other, and Clausius' entropy S in terms of the energies and available energies of the same end states. (ii) We consider the optimum shaft work done during a cyclic change of state of an engine operating between a reservoir, and a system with fixed amounts of constituents and fixed volume, but variable temperature. We express the optimum shaft work in terms of the available energies of the end states of the system, and Clausius' entropy in terms of the energies and available energies of the same end states. Formally, the entropy expression is identical to that found for the Carnot engine, except that here the change of state of the system is not isothermal. (iii) We consider the optimum shaft work done during a cyclic change of state of a general engine operating between a reservoir R and system A which initially is in any state A_1, stable or thermodynamic equilibrium or not stable equilibrium. In state A_1, the values of the amounts of constituents are n_1, and the value of the volume is V_1 whereas, in the final state A_0, $n_0 \neq n_1$ and $V_0 \neq V_1$. Using the laws of thermodynamics presented by Gyftopoulos and Beretta, we prove that such an optimum exists, call it generalized available energy with respect to R, and use it together with the energy to define a new property Σ_1. We note that the expression for Σ is formally identical to and satisfies the same criteria as Clausius' entropy S. The only difference is that Σ applies to all states, whereas Clausius' S applies only to stable equilibrium states. So we call Σ entropy and denote it by S. (iv) We use the unified quantum theory of mechanics and thermodynamics developed by Hatsopoulos and Gyftopoulos, and find a quantum theoretic expression for S in terms of the density operator ρ that yields all the probabilities associated with measurement results. (v) We note that the quantum-theoretic expression for S can be interpreted as a measure of the shape of an atom, molecule, or other system because ρ can be thought of as such a shape, and provide pictorial illustrations of this interpretation. For given values of energy E, amounts of constituents n, and volume V, the value of the measure is zero for all shapes that correspond to projectors (wave functions), positive for density operators that are not projectors, and the largest for the ρ that corresponds to the unique stable equilibrium state determined by the given E, n, and V. Accordingly, spontaneous entropy generation occurs as a system adapts its shape to conform to the internal and external forces. Beginning with an arbitrary initial ρ, this adaptation continues only until no further spontaneous change of shape can occur, that is, only until a stable equilibrium state is reached.

Introduction

Over the past few decades, we have adopted the viewpoint that the laws of thermodynamics are neither statistical nor restricted to macroscopic systems in stable or thermodynamic equilibrium states. In support of this viewpoint, we have presented both the quantum-theoretic foundations (Hatsopoulos and Gyftopoulos, 1976a, b; Beretta et al., 1984, 1985), and a nonquantal exposition of foundations and applications (Gyftopoulos and Beretta, 1991a).

Among the many novel results of the new viewpoint is the recognition that entropy is a nonstatistical property of a system, in the same sense that inertial mass, energy, and momentum are nonstatistical properties of a system, and that it is well defined for all systems, large and small, and all states, thermodynamic and nonthermodynamic equilibrium (Çubukçu and Gyftopoulos, 1994; Gyftopoulos and Çubukçu, 1997).

Most physicists and engineers find the new viewpoint, in general, and the extension of the concept of entropy to states that are not thermodynamic equilibrium, in particular, unacceptable and oppose them vehemently. To the best of our knowledge, their opposition is based solely and exclusively on the argument that the new ideas differ from the accepted dogma, and not on any experimental results or on any reasoned arguments either against our statements of the laws of thermodynamics and quantum theory, or against the faultlessly, noncircularly, and completely proven theorems, such as the theorems that result in the definition of entropy.

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Continuing our efforts to elucidate the new point of view, in this paper we present the general thermodynamic definition of entropy, S, as an outgrowth of the seminal ideas of Clausius; use the unified quantum theory of mechanics and thermodynamics developed by Hatsopoulos and Gyftopoulos and find a quantum-theoretic analytical expression for S; interpret the analytical expression as a measure of the shape of an atom, molecule, or other system as the case may warrant; provide a pictorial illustration of this interpretation; and relate shape changes to the principle of spontaneous entropy generation.

The paper is organized as follows. The Clausius definition of entropy of a reservoir is discussed in the second section; the extension of this definition to a system with variable temperature in the third section; the definition of entropy S of any system in any state in the fourth section; the quantum-theoretic analytical expression for S in the fifth section; the interpretations of a density operator as a shape of an atom, molecule, or other system, of S as a measure of such a shape, and the relation of shape changes to spontaneous entropy generation in the sixth section; and conclusions in the seventh section.

Carnot Engine

Carnot (1824) analyzed an engine X which interacts with two reservoirs A and B, and through a peculiar mode of reasoning found the correct optimum shaft work done in the course of a cyclic change of state of the engine (Fig. 1).

Using Clausius' pathfinding ideas about energy and entropy (1867), denoting energy by E, Clausius' entropy by S, temperature by T, volume by V, amounts of constituents by $\mathbf{n}$, the values of these quantities for each reservoir at the beginning and the end of the cyclic change of state of the engine by the symbols listed on Figs. 2(a) and (b), respectively, we can reproduce Carnot's seminal result by beginning with the energy and entropy balances of the composite system AXB.

Energy balance
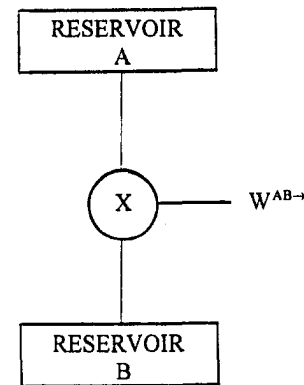
$$E_2^A - E_1^A + E_2^B - E_1^B = -W_{12}^{AB\to} \qquad (1)$$

Fig. 1 Schematic of a Carnot engine

Entropy balance

$$S_2^A - S_1^A + S_2^B - S_1^B = S_{irr} \qquad (2)$$

where $W_{12}^{AB\to}$ is the shaft work (energy transfer only) in the time interval required by the cyclic change of state of the engine, and S_{irr} the amount of entropy generated spontaneously during the same time interval. The value of $W_{12}^{AB\to}$ is positive if work is done by the engine, and negative if work is done on the engine.

For each of the reservoirs A and B, the changes of energy and Clausius entropy are proportional to each other so that

$$S_2^A - S_1^A = (E_2^A - E_1^A)/T_A \qquad (3)$$
$$S_2^B - S_1^B = (E_2^B - E_1^B)/T_B \qquad (4)$$

So, using Eqs. (2) to (4), we can eliminate the energy of reservoir B from Eq. (1) and find

$$W_{12}^{AB\to} = -(E_2^A - E_1^A)\left(1 - \frac{T_B}{T_A}\right) - T_B S_{irr} \qquad (5)$$

Because the optimum is the reversible process, and then $S_{irr} = 0$, Eq. (5) yields

--------- **Nomenclature** ---------

A = system
B = system
c_R = positive constant of reservoir R
E = energy
E^Y = energy of system Y
E_i^Y = energy of system Y in state Y_i
$\hbar$ = Planck's constant divided by 2π
l = angular momentum quantum no.
L = total angular momentum
m = z-component of angular momentum quantum no.
n = energy eigenvalue quantum no.
$\mathbf{n}$ = vector of types and amounts of constituents
$\mathbf{n}^Y$ = vector of types and amounts of constituents of system Y
$\mathbf{n}_i^Y$ = vector of types and amounts of constituents of system Y in state Y_i
S = Clausius entropy
S^Y = Clausius entropy of system Y
S_i^Y = Clausius entropy of system Y in state Y_i
S_{irr} = entropy generated spontaneously
T = temperature

T_i = temperature of system A in state A_i
T_Y = temperature of system Y
Tr = indicates trace (sum of eigenvalues) of operator that follows
V = volume
V_i^Y = volume of system Y in state Y_i
$W^{YZ\to}$ = shaft work done by composite system YZ
$W_{ij}^{YZ\to}$ = shaft work done by composite system YZ as its state changes from state $(YZ)_i$ to state $(YZ)_j$
$(W_{ij}^{YZ\to})_{rev}$ = shaft work done by composite system YZ as its state changes reversibly from state $(YZ)_i$ to state $(YZ)_j$
X = engine
ϵ_n = nth energy eigenvalue of electron in hydrogen atom
κ = Boltzmann's constant
ρ = density operator that yields all probabilities associated with measurement results

ρ_i = density operator corresponding to ith projector or wave function ψ_i
Σ^Y = entropylike property of any system Y in any state
Σ_i^Y = entropylike property of any system Y in any state Y_i
ψ_i = ith wave function
Ω^Y = available energy or exergy of system with respect to reservoir Y
Ω_i^Y = available energy or exergy of system A in state A_i with respect to reservoir Y; also generalized available energy of system A in state A_i with values $\mathbf{n}_i^A$ and V_i^A with respect to reservoir Y and final state of A with values $\mathbf{n}_0^A$ and V_0^A and such that A and Y are in mutual stable equilibrium
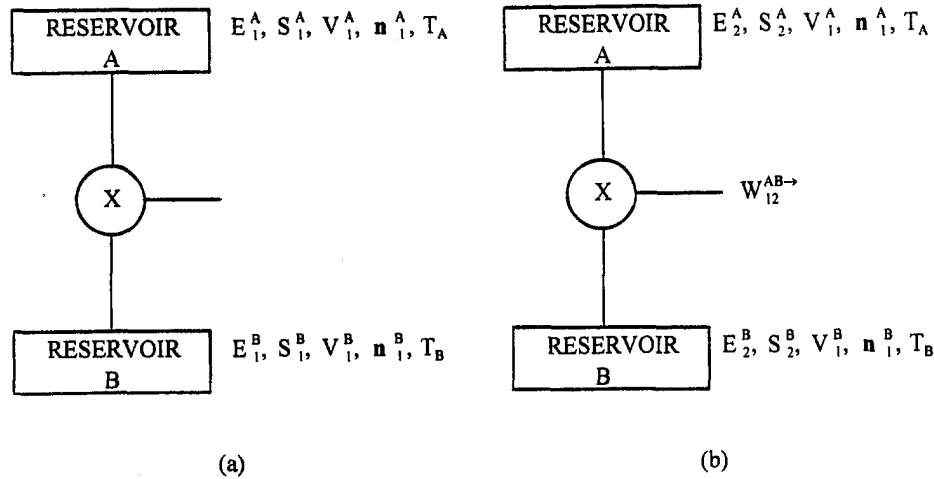
Fig. 2 Schematic of a cyclic change of state of a Carnot engine: (*a*) initial states of the reservoirs; and (*b*) final states of the reservoirs

$$(W_{12}^{AB\rightarrow})_{rev} = -(E_2^A - E_1^A)\left(1 - \frac{T_B}{T_A}\right) \qquad (6)$$

that is, Carnot's seminal result in terms of absolute temperatures, where $(W_{12}^{AB\rightarrow})_{rev}$ denotes the shaft work if the process of the composite system AXB is reversible.

For the purposes of this paper, we rewrite Eq. (6) in several equivalent forms, such as

$$(W_{12}^{AB\rightarrow})_{rev} = -(E_2^A - E_1^A) + T_B(E_2^A - E_1^A)/T_A$$

$$= -(E_2^A - E_1^A) + T_B(S_2^A - S_1^A) \qquad (7)$$

$$S_2^A - S_1^A = [(E_2^A - E_1^A) + (W_{12}^{AB\rightarrow})_{rev}]/T_B$$

$$= [(E_2^A - E_1^A) - (\Omega_2^B - \Omega_1^B)]/T_B \qquad (8)$$

where in writing the second of Eqs. (7), we use Eq. (3), the first of Eqs. (8) is a rearrangement of the second Eq. (6); and the second Eq. (8) results from the definition of Ω_i^B as the available energy or exergy of an amount of energy E_i^A of system A in state A_i at fixed temperature T_A with respect to reservoir B at temperature T_B, that is

$$\Omega_i^B = E_i^A\left(1 - \frac{T_B}{T_A}\right) \qquad (9)$$

As is very well known, the available energy or exergy Ω_i^B is a property of both system A and reservoir B. It is noteworthy, however, that both the entropy S_i^A and the energy E_i^A are independent of reservoir B. We can express this important result in another way. We consider the same changes of energy and entropy of system A from state A_1 to state A_2, but in a process of a composite system AXR consisting of system A, engine X, and reservoir R at temperature T_R. In the course of a cycle of X, we can readily verify that

$$S_2^A - S_1^A = [(E_2^A - E_1^A) - (\Omega_2^R - \Omega_1^R)]/T_R \qquad (10)$$

where Ω_i^R is the available energy or exergy of E_i^A at fixed temperature T_A with respect to a reservoir at temperature T_R, that is

$$\Omega_i^R = E_i^A\left(1 - \frac{T_R}{T_A}\right) \qquad (11)$$

Though Ω^R and T_R depend on the reservoir, we see from Eq. (10) that neither E^A nor S^A has this dependence.

Engine Operating Between a System That Can Assume Different Temperatures and a Reservoir

Next, we consider a cyclic change of state of an engine X while it interacts with system A and reservoir R so that the values of E, T, V, $\mathbf{n}$, and Clausius' entropy S of the end states of A and R are as listed on Figs. 3(*a*) and (*b*). In contrast to the process depicted in Fig. 2, here the initial temperature of A is T_1, and the final temperature $T_0 = T_R$, that is, at the end of the process, system A is in mutual stable equilibrium with reservoir R.

If the process of the composite system AXR is reversible, the energy transferred through the shaft $(W_{10}^{AR\rightarrow})_{rev}$ is optimum, the energy and Clausius' entropy that flow out of system A are $E_0^A - E_1^A$ and $S_0^A - S_1^A$, respectively, and transfer of the entropy $S_0^A - S_1^A$ into reservoir R at the end of the cyclic change of state of X requires the concurrent transfer of energy $T_R(S_0^A - S_1^A)$ (Eq. (4)). So the energy balance for the composite system AXR yields

$$(W_{10}^{AR\rightarrow})_{rev} = -[(E_0^A - E_1^A) - T_R(S_0^A - S_1^A)] \qquad (12)$$

or, equivalently,

$$S_1^A - S_0^A = [(E_1^A - E_0^A) - (W_{10}^{AR\rightarrow})_{rev}]/T_R$$

$$= [(E_1^A - E_0^A) - \Omega_1^R]/T_R \qquad (13)$$

where $\Omega_1^R = (W_{10}^{AR})_{rev}$. It is clear that Ω_1^R is a property of both system A and reservoir R, and represents the largest work that can be done by the composite system AXR as A starts from an initial stable or thermodynamic equilibrium state A_1 and ends in a stable or thermodynamic equilibrium state A_0 such that A and R are in mutual stable equilibrium, and X undergoes a cyclic change of state. By definition, this work is the available energy or exergy of state A_1 with respect to reservoir R.

If during the cyclic change of state of X, the reversible process of the composite system AXR starts with system A in stable equilibrium state A_1 and ends with A in stable equilibrium state A_2 different from A_0, then repeated application of Eq. (13) yields

$$S_2^A - S_1^A = [(E_2^A - E_1^A) - (\Omega_2^R - \Omega_1^R)]/T_R \qquad (14)$$

Though in Eqs. (13) and (14), both Ω^R and T_R depend on R, it is noteworthy that neither energy E^A nor Clausius entropy S^A exhibit such dependence.

The Clausius entropy appearing in Eqs. (10) and (14) can be shown to satisfy the following conditions (Callen, 1985):
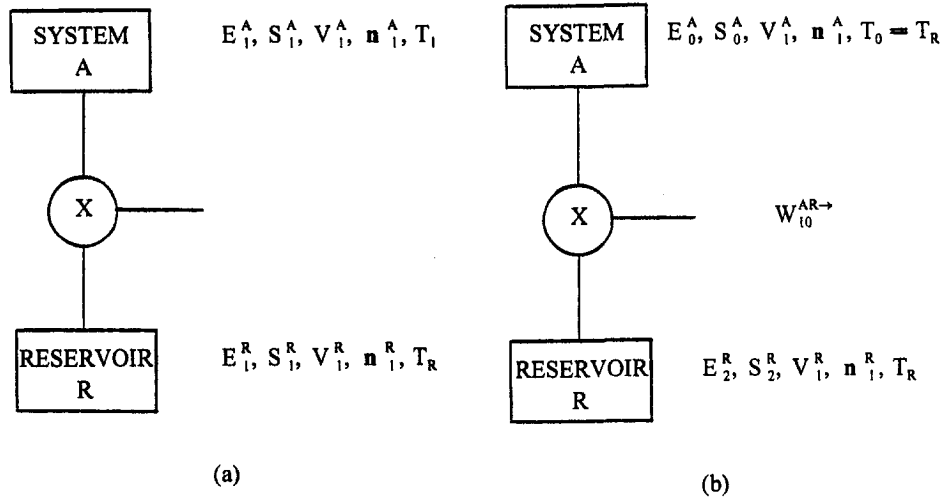
SYSTEM A $E_1^A, S_1^A, V_1^A, n_1^A, T_1$

X

RESERVOIR R $E_1^R, S_1^R, V_1^R, n_1^R, T_R$

(a)

SYSTEM A $E_0^A, S_0^A, V_1^A, n_1^A, T_0 = T_R$

X $W_{t0}^{AR\to}$

RESERVOIR R $E_2^R, S_2^R, V_1^R, n_1^R, T_R$

(b)

Fig. 3 Schematic of a cyclic change of state of an engine: (a) Initial state of A at temperature T_1; and (b) final state of A at temperature $T_0 = T_R$

1 It applies to stable or thermodynamic equilibrium states only.
2 It is independent of the reservoir.
3 It is nondecreasing in adiabatic processes.
4 It is additive.
5 It can be assigned non-negative values only.
6 For given values of energy, volume, and amounts of constituents, it assumes a maximum.
7 For given values of volume and amounts of constituents, the graph of S versus E is concave.
8 For mutual stable equilibrium between two systems, it yields the conditions of temperature equality, total potential equalities, and pressure equality.

In addition to these conditions, a scarcely appreciated fact is that the Clausius entropy applies to all systems, large and small, and is not statistical because neither Clausius nor other scientists that worked on the foundations and theorems of the theory of classical thermodynamics made any restrictive assumptions either about the size of the system or about the phenomena explained by this theory being statistical, or both. Beginning with Maxwell and Boltzmann, restrictive assumptions are introduced only by scientists who wish to explain thermodynamic phenomena by means of statistical mechanical theories, either classical or quantum.

A General Engine

Next, we consider an engine X that interacts with system A and reservoir R, and does shaft work under the conditions listed on Fig. 4. Initially, A is in state A_1, which is not necessarily thermodynamic equilibrium. In this state, the values of the amounts of constituents are n_1^A, and the value of the volume is V_1^A (Fig. 4(a)). At the end of the interactions, engine X has undergone a cyclic change of state and has done shaft work $W_{10}^{AR\to}$, and the state of A has changed from A_1 to a thermodynamic equilibrium state A_0. The latter state corresponds to prespecified values V_0^A of the volume and n_0^A of the constituents, and is such that A and R are in (partial) mutual stable equilibrium (Fig. 4(b)).

Using their statements of the laws of thermodynamics[1] (see Appendix), Gyftopoulos and Beretta (1991b) prove that if the process of AXR just cited is reversible, then the engine shaft work is optimum—the largest if done by the cyclic engine or the smallest if done on the cyclic engine. They call this optimum shaft work *generalized available energy* of state A_1 with respect to reservoir R and the values n_0^A and V_0^A and, for the sake of simplicity of nomenclature, denote it by the same symbol Ω_1^R as that for available energy. It is noteworthy that, under the proper conditions, generalized available energy reduces to the available energy or exergy concept represented by either Eq. (11) or the definition in Eq. (13).

Next, Gyftopoulos and Beretta establish several characteristic features of generalized available energy with respect to a fixed reservoir R. For example, they consider two arbitrary states A_1 and A_2 of system A, and a state A_0 with prespecified values n_0^A and V_0^A and such that A and R are in (partial) mutual stable equilibrium. For an adiabatic process from A_1 to A_2 of system A only, they show that the energy difference $E_1^A - E_2^A$ of A and the generalized available energy difference $\Omega_1^R - \Omega_2^R$ of the composite of A and R satisfy the following relations:

If the adiabatic process of A is reversible

$$E_1^A - E_2^A = \Omega_1^R - \Omega_2^R \qquad (15)$$

If the adiabatic process of A is irreversible

$$E_1^A - E_2^A < \Omega_1^R - \Omega_2^R \qquad (16)$$

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,[2] or whether the size of the system is large or small.

Next, we define the following linear combination of energy and generalized available energy:

$$\Sigma_2^A - \Sigma_1^A = [(E_2^A - E_1^A) - (\Omega_2^R - \Omega_1^R)]/c_R \qquad (17)$$

where c_R is a positive constant which can be chosen so as to make Σ independent of R. The proof that such a choice of c_R is possible is given by Gyftopoulos and Beretta (1991c). It turns out that the value of c_R is also equal to the temperature T_R of the reservoir.

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[1] All correct statements of the laws of thermodynamics that appear in the literature are proven to be special cases of the statements given by Gyftopoulos and Beretta (1991a).

[2] For a molecule, the degrees of freedom refer to the independent variations that can be made in the spatial coordinates which specify the position and configuration of the molecule. They are classified as translational, rotational, vibrational, and electronic.
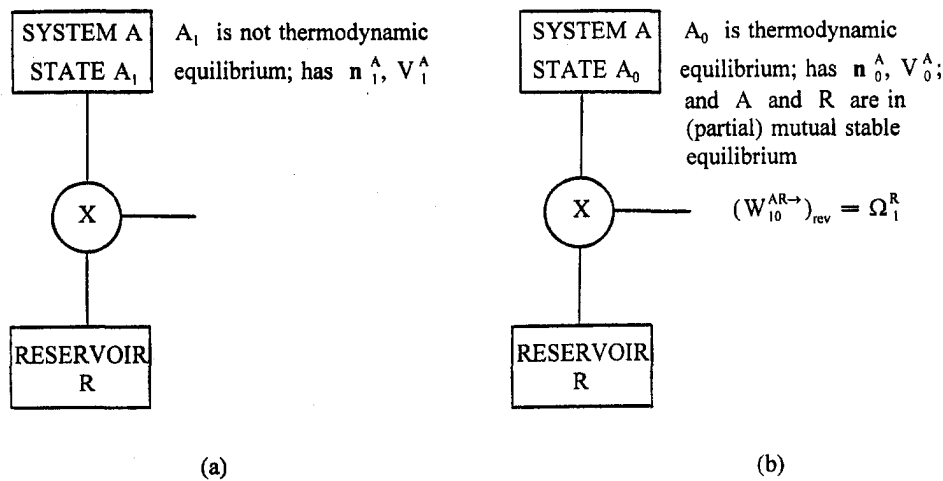
Fig. 4 Schematic of a cyclic change of state of an engine: (a) initial state of A is not thermodynamic equilibrium; and (b) final state of A is thermodynamic equilibrium so that A and R are in (partial) mutual stable equilibrium

Based on the proven characteristic features of E and Ω^R, we find that Σ satisfies the following conditions:

1. For the specifications of either the Carnot engine or the engine operating between a system that can assume different temperatures and a reservoir, Σ satisfies either Eq. (10) or (14), respectively.
2. It is well defined for all systems and all states.
3. It is independent of R.
4. It is nondecreasing in adiabatic processes (see Eqs. (15) and (16)).
5. It is additive because both E and Ω^R are proven to be additive (Gyftopoulos and Beretta, 1991d).
6. It can be assigned non-negative values (Gyftopoulos and Beretta, 1991e).
7. Among all the states of a system having given values of energy, volume, and amounts of constituents, there exists only one which has the largest Σ (see second law statement in Appendix).
8. For given values of volume and amounts of constituents, the graph of Σ versus E of the stable or thermodynamic equilibrium states (largest-Σ states) is concave (Gyftopoulos and Beretta, 1991f).
9. For mutual stable equilibrium between two systems, Σ yields the conditions of temperature equality, total potential equalities, and pressure equality (Gyftopoulos and Beretta, 1991g).

Comparison of this list with the list of characteristic features of Clausius' entropy for stable or thermodynamic equilibrium states indicates that Σ behaves exactly like the Clausius entropy, maintains these characteristics for states that are not thermodynamic equilibrium, and is nonstatistical.

It is alleged that the late Cardinal Cushing of Boston said "When I see a bird that walks like a duck, swims like a duck, and quacks like a duck, I call that bird a duck." Though a non-Catholic, but a Bostonian over the past 44 years, I believe that the comparison of the characteristic features of Clausius' entropy and those of Σ allows us to paraphrase the late Cardinal's alleged statement and aver with a very high degree of certainty that both states which are not thermodynamic equilibrium, and states which are thermodynamic equilibrium can be assigned entropy, and that this entropy is defined by Eq. (17) for $\Sigma^A = S^A$.

Quantum Theoretic Expression of Entropy

Ever since the enunciation of the first and second laws of thermodynamics by Clausius more than 130 years ago, all ex-

pressions 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 reality), 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 a system.

Over the past three decades, a different point of view has emerged consistent with the idea that entropy is a property of a system. Hatsopoulos and Gyftopoulos (1976b) observed that the von Neumann concept of an unambiguous or homogeneous ensemble of identical systems that represents a density operator equal to a projector (every member of the ensemble is assigned the same projector, $\rho_i = \rho_i^2$, or the same wave function ψ_i as any other member) can be readily extended to density operators that are not projectors. Thus, every member of the ensemble is assigned 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 radical changes of the quantum-theoretic postulates about observables, measurement results, and values of observables. An identical conclusion is reached by other scientists (Jauch, 1973).

As is very well known, at an instant in time, a specific projector ρ_i or, equivalently, wave function ψ_i, is the seat only of all quantum probabilities of measurement results. The measurements are performed on a homogeneous ensemble of identical systems, identically prepared for the instant in time under consideration.

Similarly, at an instant in time, a specific density operator ρ ($\rho > \rho^2$) is the seat only of all quantum probabilities of measurement results of measurements performed on an unambiguous or homogeneous ensemble of identical systems, identically prepared for the instant in time under consideration. The relation between the density operator and the probability of a measurement result is discussed in every good textbook on quantum theory.

In sharp contrast to statistical quantum mechanics, it is noteworthy that density operators used in our work represent only quantum probabilities inherent to the nature of physical reality, and not mixtures of statistical probabilities accounting for our ignorance and inability to perform complicated calculations, and quantum probabilities represented by projectors and accounting for phenomena inherent to the nature of physical reality.

One benefit of the recognition that density operators $\rho >$ ρ^2 are encompassed by the quantum-theoretic postulates is the elimination of the monstrosity of the concept of mixed state that concerned Schroedinger (1936) and Park (1968, 1988). Another even more important benefit is that the recognition 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 (Hatsopoulos and Gyftopoulos, 1976a).

Combining the laws of thermodynamics given by Gyftopoulos and Beretta (see Appendix), and the postulates of the unified quantum theory of mechanics and thermodynamics developed by Hatsopoulos and Gyftopoulos (1976a, b), Gyftopoulos and Çubukçu (1997) show that the only known quantum expression that complies with all the conditions that must be satisfied by the entropy of thermodynamics is

$$S = -\kappa \ \mathrm{Tr} \ \rho \ \ln \rho \qquad (18)$$

that is, the product of Boltzmann's constant k and the trace (Tr) of the operator $\rho \ \ln \rho$, and of course only if ρ corresponds to a homogeneous ensemble and not to a statistical mixture of either projectors or other nonprojector density operators ($\rho_k \neq \rho$) because only ρ's that correspond to homogeneous ensembles are subject to the laws of physics.

Pictorial Illustration of Entropy

In conventional quantum mechanics in which all probabilities associated with measurement results are represented by projectors or, equivalently, by wave functions, we interpret the probability density function in the spatial language as the shape of an atom, molecule, or other system as the case warrants (Leighton, 1959; Slater, 1963; and Brandt and Dahmen, 1995), and use the shape to visualize charge distributions, to calculate atomic and molecular radii, and to explain the formation of polyatomic molecules.

A few pictures of surfaces of constant probability density of energy eigenfunctions (energy eigenprojectors) of the electron in a hydrogen atom calculated by Brandt and Dahmen (1995) are shown in Figs. 5 and 6. In the notation $\rho_{n\ell m}$ of each shape, subscript n denotes the energy quantum number and appears in the energy eigenvalue relation

$$\epsilon_n = -13.61/n^2 (eV) \qquad (19)$$

subscript l denotes the angular momentum quantum number ($0 \leq 1 \leq n - 1$) and appears in the square of the total angular momentum eigenvalue relation

$$L^2 = \hbar^2 l(1 + 1) \qquad (20)$$

where L^2 is the square of the total angular momentum, and $\hbar$ Planck's constant divided by 2π, and subscript m denotes the z-component of the angular momentum quantum number ($-\ell \leq m \leq 1$) and appears in eigenvalue relation

$$L_z = m\hbar \qquad (21)$$

where L_z is the z-component of the angular momentum.

The energy eigenfunctions of a given system form a complete orthonormal set. They can be superimposed—be combined in a series—to represent any wave function ψ, and therefore, all the probability distributions of measurement results contemplated in conventional quantum mechanics. In the sense illustrated in Figs. 5 and 6, each of these distributions has its own shape.

To each wave function there corresponds a projector or density operator $\rho_i = \rho_i^2$. The discussion of the relation between a wave function and its projector is beyond the scope of this paper. It is presented in many textbooks (Louisell, 1973; Kroemer, 1994).
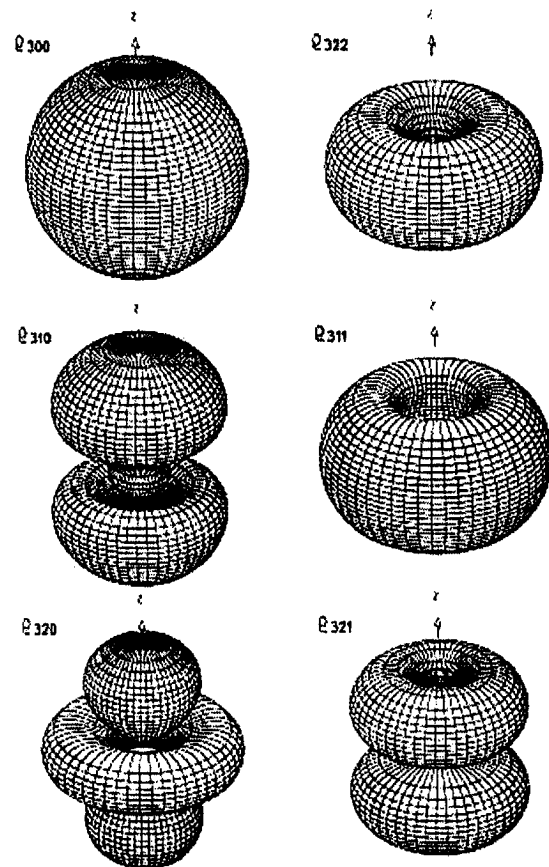

Fig. 5 Surfaces of constant probability density $\rho_{2\ell m}$ = 0.0002 in full x, y, z-space of the electron in a hydrogen atom (from Brandt and Dahmen, 1995)

For our purposes, it suffices to state that a set of orthonormal wave functions can be transformed into a complete set of projectors, and that an appropriate complete set of projectors can be superimposed—be combined in a series—to represent a density operator $\rho > \rho^2$. Thus, the probability distributions contemplated in the unified quantum theory of mechanics and thermodynamics can be fully covered. And again in the sense of Figs. 5 and 6, each of the probability distributions arising from a given $\rho > \rho^2$ has its own shape.

As a result of the interpretation of any density operator as representing the shape of an atom, molecule, or other system, we can consider the quantum expression of entropy (Eq. 18) as a special measure of the shape of an atom, molecule, or other system as the case requires. For given values of the energy E, volume V, and amounts of constituents $\mathbf{n}$, the values of the special measure S range from zero to a maximum. For all density operators that are projectors, $\rho_i = \rho_i^2$, the value of $S = 0$. For all other density operators, $\rho > \rho^2$, $S > 0$ and reaches the largest value for the density operator ρ° that corresponds to the unique stable equilibrium state dictated by the second law of thermodynamics for the given values E, V, $\mathbf{n}$.

With this interpretation in mind, we can think of the spontaneous increase of entropy in the course of irreversible processes as a natural tendency of an atom, molecule, or other system to adapt the shape of its state to the nest of internal and external forces of the system until no further reshaping is possible, that is, until the largest value of S for given values of E, V, and $\mathbf{n}$ is achieved. The adaptation to the internal and external forces is beautifully visualized by considering the spontaneous expansion of an amount of colored gas squirted in a corner of a transparent glass container.
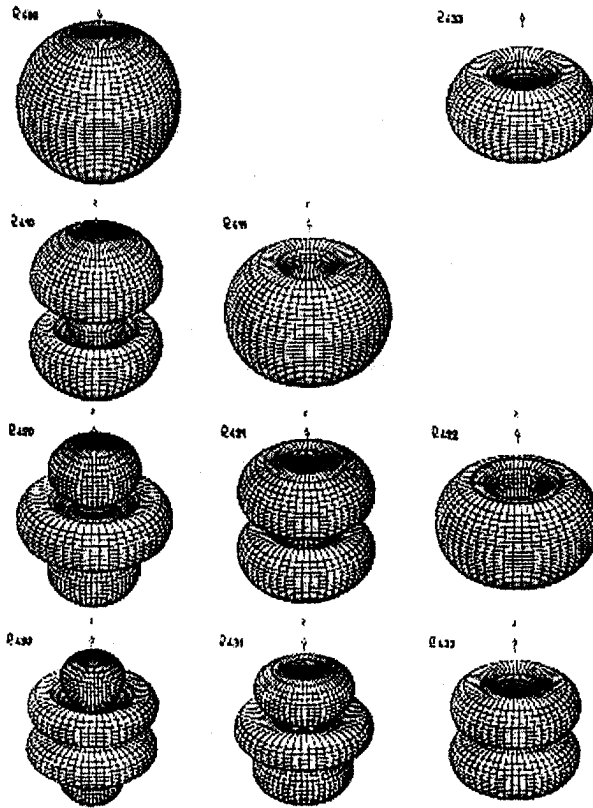
Fig. 6 Surfaces of constant probability density $\rho_{4\ell m} = 0.00002$ in full x, y, z-space of the electron in a hydrogen atom (from Brandt and Dahmen, 1995)

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If it occurs, the spontaneous increase of S is detrimental because, as a nondestructible and nonstatistical property of a system, entropy cannot be returned to some small initial value without compensation, that is, without transfer of entropy to the environment.

Conclusions

By using only the concepts of space, time, and inertial mass or force, and the laws of thermodynamics (see Appendix), Gyftopoulos and Beretta (1991a) disclosed the existence of entropy as a nonstatistical property of any system in any state. By combining the laws of thermodynamics with the postulates of quantum theory, Gyftopoulos and Çubukçu (1997) proved that the only known expression that represents entropy is $S = -k\mathrm{Tr}\rho \ln \rho$. By associating ρ with the shape of an atom, molecule, or other system, entropy is interpreted as a nondestructible measure of that shape, and spontaneous generation of entropy as the increase of the measure as the spatial shape of the system tumbles to adapt itself to the internal and external forces.

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APPENDIX

The Laws of Thermodynamics

Gyftopoulos and Beretta state the laws of thermodynamics as follows:

First Law: Any two states of a system may always be the end states of a weight process, that is, the initial and final states of a change of state that involves no net effects external to the system except the change in elevation between z_1 and z_2 of a weight. Moreover, for a given weight, the value of the quantity Mg ($z_1 - z_2$) is fixed by the end states of the system, and independent of the details of the weight process, where M is the mass of the weight and g the gravitational acceleration.

Second Law (simplified version): Among all the states of a system with a given value of the energy, and given values of the amounts of constituents and volume, there exists one and only one stable equilibrium state.

Third Law (simplified version): For each given set of values of the amounts of constituents and the volume of a system, there exists one stable equilibrium state with zero temperature.