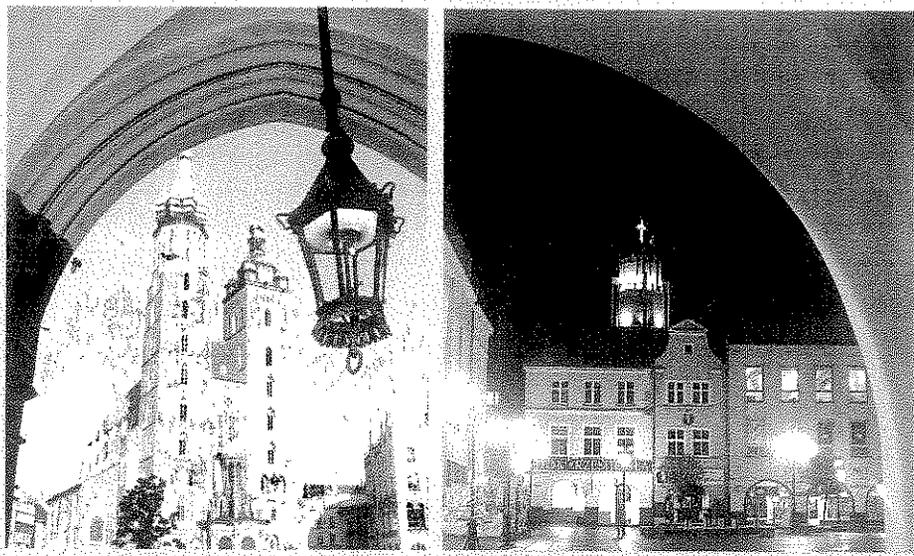


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Andrzej Ziębik, Zygmunt Kolenda, Wojciech Stanek

## **Keynote lectures**

# Thermodynamics

Elias P. Gyftopoulos

*Massachusetts Institute of Technology, Massachusetts USA*

## Abstract

A large number of textbooks and articles on thermodynamics, and classical or quantum physics claim that thermodynamics is a statistical theory applicable only to systems consisting of very large numbers of particles in thermodynamic equilibrium states, entropy is defined as a measure of ultimate disorder and not as a physical property of the system, and disorder is defined as representing motions of particles with different velocities both in values and in directions.

The purpose of this article is to show and emphasize once more that none of these claims is valid for the following reasons: Thermodynamics is a science that: (i) applies to all systems, regardless of whether they consist of one spin, one particle, or any number of constituents of any kind, and to all states, regardless of whether the state is unsteady, steady, nonequilibrium, different types of equilibrium, or stable (thermodynamic) equilibrium; (ii) entropy is a nonstatistical physical property of any system in any state, in the same sense that energy is a nonstatistical physical property of any system in any state; and (iii) any stable equilibrium state is a state of ultimate order.

Similar comments apply to thermodynamics in its quantum form but are not included for the sake of brevity.

## 1. Introduction

I noticed that the first scientific term in the announcement of this conference is THERMODYNAMICS. So, I think it is useful to take advantage of the opportunity and review the nonquantum foundations of the subject, as well as some practical and challenging applications.

Given that many ideas about thermodynamics were introduced in the 19<sup>th</sup> and early 20<sup>th</sup> centuries, we might have assumed that there is little controversy about its foundations and applications. However, even a cursory review of the relevant literature shows that this is not the case. The ideas of thermodynamics have been the subject of controversy ever since their inception [1], controversy that continues even today. Though dated, the following comments continue to be claimed. Obert [2] writes: “Most teachers will agree that the subject of engineering thermodynamics is confusing to the student despite the simplicity of the usual undergraduate presentation”. Again, Tisza [3] states: “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”. Werhl [4] 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”. Lindblad [5] gives a large number of different expressions for entropy and comments: “The entropy function is not

unique. Instead there is a family of such functions, one for each set of thermodynamic processes allowed by the experimenter's control of the dynamics of the system through the external fields. This scheme is in line with the philosophy described by Jaynes' dictum: Entropy is a property, not of the physical system, but of the particular experiments you or I choose to perform on it." Truesdell [6] identifies several different statements of the second law. Mehra and Sudarshan [8] among many other very important recommendations declare: "We maintain that for the explanation of statistical mechanical phenomena the law of evolution is not Hamiltonian, and by creating a generalized dynamics which is essentially non-Hamiltonian we can rid ourselves of all *ad hoc* intermediate assumptions. Thereby we can also shed all the paradoxes that arise in connection with Boltzmann's equation and the *H*-theorem, as well as the pretense of the mechanical explanation of the second law of thermodynamics".

It is noteworthy that the recommendation just cited was made also by Sadi Carnot [9] more than a century and a half earlier in his pioneering and trail blazing "*Reflections on the motive power of fire*". He said: "In order to consider in the most general way the principle of the production of motion by heat, it must be considered independently of any mechanism or any particular agent. It is necessary to establish principles applicable not only to steam engines but to all imaginable heat engines, whatever the working substance and whatever the method by which it is operated."

And then Carnot continues: "Machines which do not receive their motion from heat ... can be studied even to their smallest details by the mechanical theory. All cases are foreseen, all imaginable movements are referred to these general principles ... . This is the character of a complete theory. A similar theory is evidently needed for heat engines. We shall have it only when the laws of physics shall be extended enough, generalized enough, to make known before hand all the effects of heat acting in a determined manner on any body".

About forty years ago, a group at MIT began a response to the concerns just cited which we describe 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 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 of a unified quantum theory of mechanics and thermodynamics, and Beretta et al [12, 13] discovered a complete equation of motion for the unified quantum theory just cited. Both quantum mechanical developments involve only quantum mechanical probabilities and no statistical probabilities of the types used in either statistical classical mechanics, or statistical quantum mechanics.

In what follows, I present only the foundations of the new theory of thermodynamics without reference to quantum mechanics.

## **2. Thermodynamics**

### *2.1 General remarks*

In this section, I outline the exposition of the foundations of thermodynamics discussed in Ref. [10]. 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; first law (without energy, work, and heat); 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 in terms of energy and generalized available energy; entropy balance; fundamental relation for stable equilibrium states only; temperature, total potentials (chemical and/or electrochemical), and pressure in terms of energy, entropy, amounts of constituents and parameters for stable equilibrium states only; third law; work in terms of energy; heat in terms of energy, entropy, and temperature; and availability or exergy.

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

## 2.2 Definition

We define *general thermodynamics* or simply *thermodynamics* as the study of motions of physical constituents (particles, spins, and radiations) resulting from externally applied forces, and from internal forces (actions on and reactions between constituents). 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.

## 2.3 Kinematics: conditions at an instant in time

In our exposition, 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 attributable to lack of either computational abilities, or lack of information about any aspect of a problem in physics, and/or consideration of numerical and computational difficulties. The definitions include innovations. To the best of our knowledge, they violate no theoretical principle, and contradict no experimental results.

A *system* is defined as a collection of *constituents*, subject to both *internal forces*, that is, forces between constituents, and *external forces*. Everything that is not included in the system is the *environment*. Two very important requirements for the definitions of system and environment to be valid are that the system be both separable from and uncorrelated with its environment.

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

At any instant in time, the amounts of the constituents 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 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 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 the constituents, the values of the parameters, and the values of a complete set of linearly 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 any instant in time the *state* of the system. This definition of state, without change, applies to all paradigms of physics.

#### 2.4 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 – *spontaneous changes of state* – or of a system subject to forces that do not violate the definition of the system is the *equation of motion*. Certain time evolutions obey Newton’s equation which relates the force  $F$  on each system particle to its mass  $m$  and acceleration  $a$  so that  $F = ma$ . Other evolutions obey the Schrödinger equation, that is, the quantum-mechanical equivalent of Newton’s equation. In this essay I will not discuss the general equation of motion except to note that 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 three laws of thermodynamics discussed later and their consequences.

#### 2.5 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 from  $z_1$  to  $z_2$  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. Many other mechanical effects can be used in the statement of the first law instead of the weight.

The main consequence of this law is that every system  $A$  in state  $A_1$  has a property called *energy*, with a value denoted by the symbol  $E_1$ . 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

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

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 that energy remains invariant in time if the process is spontaneous. 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. [10], this result is obtained without use of the complete 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 derive the *energy balance*. This derivation is based on the additivity of energy and energy conservation, and reads

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

In words, the energy change of a system must be accounted for by the energy transferred across the boundary of the system, and the arrow indicates that  $E^{A\leftarrow}$  is positive if energy is transferred into the system.

## 2.6 Types of states

Because the number of independent properties of a system may be infinite even for a system consisting of a single particle with a single translational degree of freedom – a single dimension in which the particle is allowed to move – 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 other systems in the environment. A *nonequilibrium state* is one that changes spontaneously as a function of time, that is, a state that evolves in time without any effects on or interactions with any systems in the environment. An *equilibrium state* is one that does not change in 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 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 broader spectrum of states than those encountered in mechanics. The broader spectrum is due to both the first law and the second law discussed later.

Starting either from a nonequilibrium state or from an equilibrium state that is not stable, experience shows that energy can be transferred out of the system 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.

### 2.7 The second law and generalized available energy

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 (simplified version): 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].

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, i.e. to increase the energy of another system, 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 many expositions of thermodynamics, it is erroneously 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  $\Psi$  [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  $\mathbf{n}_1'$ ,  $\beta_1'$ , and ends in a state  $A_2''$  with values  $\mathbf{n}_2''$ ,  $\beta_2''$ . Like energy, this property is well defined for all systems and all states, but unlike energy it is not additive [10]. In striving to define an additive property that captures the important features of generalized adiabatic availability, Gyftopoulos and Beretta [10] introduce a special reference system  $R$ , called a *reservoir*, and discuss the possible weight processes that the composite of  $A$  and  $R$  may experience as  $A$  changes from state  $A_1'$  to  $A_2''$ . Thus they disclose another 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 the composite – the optimum mechanical effect. They call the optimum value *generalized available energy*, denote it by  $\Omega^R$ , and show that it is additive, and 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. [10].

For an *adiabatic process* of system  $A$  only, that is, a process during which the only effect on  $A$  is a change of its energy, 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 [10]. If the adiabatic process of  $A$  is reversible,

$$E_1 - E_2 = \Omega_1^R - \Omega_2^R \quad (3)$$

If the adiabatic process of  $A$  is irreversible,

$$E_1 - E_2 < \Omega_1^R - \Omega_2^R \quad (4)$$

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. In either process, the restoration path need not and usually does not coincide with the reverse of the initial sequence of states.

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, nonequilibrium, equilibrium, or stable equilibrium, and regardless of whether the system has many degrees of freedom or one degree of freedom, or whether the number of constituents and/or the volume of the system are large or small.

### 3. Entropy

#### 3.1 Definition

A system  $A$  in any state  $A_1$  has many properties. Two of these properties are energy  $E_1$  and generalized adiabatic availability  $\Psi_1$ . Also a composite of a system  $A$  and a reservoir  $R$  has many properties. One of these properties is *generalized available energy*  $\Omega^R$  with respect to the given reservoir  $R$ . The two properties  $E$  and  $\Omega^R$  determine a property of  $A$  only, which is called *entropy*, and denoted by the symbol  $S$ . For state  $A_1$ ,  $S_1$  can be evaluated by means of any reservoir  $R$ , a reference state  $A_0$  to which we assign arbitrary values of energy  $E_0$ , entropy  $S_0$ , and generalized available energy  $\Omega_0^R$ , and the expression:

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

where  $c_R$  is a well-defined positive constant that in due course will be shown to depend only on the auxiliary reservoir  $R$ . Entropy  $S$  is shown to be independent of the reservoir, that is,  $S$  is an inherent – intrinsic – property of system  $A$  like energy  $E$  is an inherent property of  $A$ , and the

reservoir is auxiliary and 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, quantum or other.

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 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. (5) 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

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

where  $S_{\text{irr}}$  is non-negative. A positive  $S_{\text{irr}}$  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 later. From Eq. 5, it follows that the dimensions of  $S$  are energy over temperature.

### 3.2 Stable equilibrium states

Among the many states of a system that have given values of energy  $E$ , amounts of constituents  $\mathbf{n}$ , and parameters  $\boldsymbol{\beta}$ , it is shown that 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  $\boldsymbol{\beta}$  [10], and can be expressed as a function

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

Equation (7) is called the *fundamental relation*, and may also be expressed in the form  $E = E(S, \mathbf{n}, \boldsymbol{\beta})$ .

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

$$\left[ \frac{\partial^2 S}{\partial E^2} \right]_{\mathbf{n}, \beta} \leq 0 \quad (8)$$

Moreover, the fundamental relation is used to define other properties of stable equilibrium states, such as *temperature*  $T$

$$\frac{1}{T} = \left[ \frac{\partial S}{\partial E} \right]_{\mathbf{n}, \beta} = \frac{1}{(\partial E / \partial S)_{\mathbf{n}, \beta}} \quad (9)$$

*total potentials*  $\mu_i$

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

*and pressure*  $p$

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

The temperature, total potentials, and pressure of a stable equilibrium state appear in the necessary conditions for systems to be in mutual stable equilibrium, 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  $T$ ,  $\mu_i$ 's, and  $p$ .

The ranges of values of  $T$ ,  $\mu_i$ '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 one or 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  $-\infty$ . So, for such systems the range of temperature is  $-\infty < 1/T < \infty$ .

### 3.3 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

$$E_{\text{final}} - E_{\text{initial}} = \Delta E_{\text{system}} = -W^{\rightarrow} \quad (12)$$

$$S_{\text{final}} - S_{\text{initial}} = \Delta S_{\text{system}} = S_{\text{irr}} \quad (13)$$

where the arrow indicates that  $W^{\rightarrow}$  is positive if energy flows out of the system, and therefore the energy of the system decreases, and  $S_{\text{irr}} \neq 0$  and is positive if the process is irreversible, and  $S_{\text{irr}} = 0$  if the process is reversible.

*Heat* is an interaction in which the system exchanges only energy and entropy with a reservoir in its environment and nothing else. 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 of its energy. Thus, for a system experiencing only a heat interaction, the energy and entropy balances are

$$\Delta E_{\text{system}} = Q^{\leftarrow} \quad (14)$$

$$\Delta S_{\text{system}} = Q^{\leftarrow}/T_R + S_{\text{irr}} \quad (15)$$

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 [10], Chapters 8-12.

### 3.4 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.
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; and (b) all the criteria (1) to (8) are important in the determination of the analytical expression of entropy in quantum thermodynamics.

### 3.5 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, 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 stable equilibrium and all other types of states because energy and generalized available energy are defined for all states; and most certainly, it is not statistical – it is an intrinsic 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. Despite these differences, for thermodynamic equilibrium states we can verify that the entropy defined by Eq. 5 has the same values as those listed in existing tables of properties of different substances.

To emphasize the difference and generality of the new concept of entropy, we recall contrary statements by: (a) 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”; (b) 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”<sup>†</sup>; and (c) by Lieb and Yngvason [19]: “Once again it is a good idea to try to understand first the meaning of entropy for equilibrium states – the quantity that our textbooks talk about when they draw Carnot cycles. In this article we restrict our attention to just those states”. It is noteworthy, that even from their totally unjustified and limited perspective, Lieb and Yngvason introduce 16 axioms in order to explain their second law of thermodynamics [20].

<sup>†</sup>In Callen’s terminology, equilibrium state means thermodynamic equilibrium state. The same terminology is used in [19].

#### 4. Energy versus Entropy Graphs

Because they are defined in terms of the values of the amounts of constituents, the parameters, and a complete set of independent properties, states can in practice be represented by points in a multidimensional geometrical space with one axis for each amount, parameter, and independent property. Such a representation, however, would not be enlightening because the number of independent properties of most systems is very large. Nevertheless, useful information can be summarized by projecting the multi-dimensional space onto a three or two dimensional space corresponding to two or three properties.

In this article, I discuss only the energy versus entropy graph, Fig. 1, that illustrates many useful implications of thermodynamics. For any system without upper limit on energy, the projection has the shape of the area between the zero entropy axis and the curve of the stable equilibrium states. It is noteworthy that each point of the curve is the projection of one and only one stable equilibrium state, in contrast to the zero entropy line and the cross-hatched area where each point represents the projection of an infinite number of states. Many conclusions that can be inferred from energy versus entropy graphs are discussed in [10]. Here I will comment only on two interesting implications.

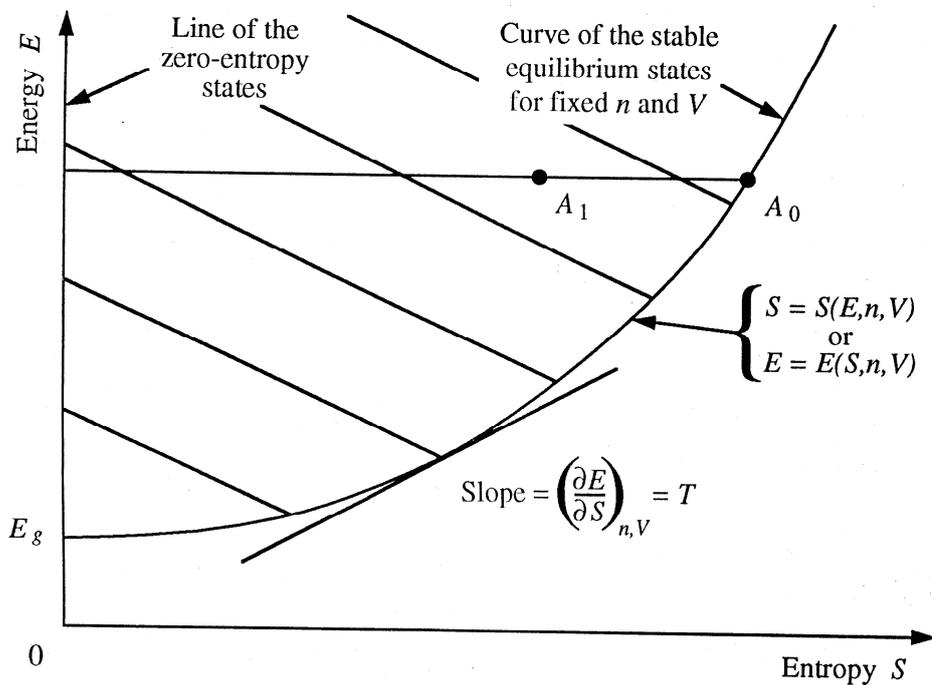


Figure 1. Projection of the multidimensional property space on the energy versus entropy plane. Except for the curve, every other point of the graph represents the projection of an infinite number of states. Every point of the curve represents one and only one stable (thermodynamic) equilibrium state.

Maxwell conceived an omniscient and omnipotent being [21], named by Thomson [22] a demon, that at no cost whatsoever could separate fast from the slow molecules of a gaseous system in a thermodynamic equilibrium state, and thus extract energy only, i.e., achieve a work interaction with other systems. This conception was motivated solely by Maxwell's conviction that, at the microscopic level, air molecules in a container and in a thermodynamic equilibrium state obey exclusively the laws of classical mechanics, and move in all directions with different velocities. The exposition of thermodynamics summarized in this essay reveals two reasons each of which indicates that the extraction of energy only from a system in a thermodynamic equilibrium state is impossible. We can prove this assertion by considering the projection of the multidimensional space onto the two-dimensional plane of energy versus entropy, Figure 1. Starting from a thermodynamic equilibrium state  $A_0$ , the separation of the gaseous molecules into fast and slow without any cost to the demon implies that at the end of the separation the state would have the same energy but would be  $A_1$ , i.e., a state of smaller entropy. But such a reduction is impossible because entropy is a nondestructible property of any system. Alternatively, the demon cannot accomplish his task at no energy cost and no entropy change because there are no states of lower energy below state  $A_0$ . For complete discussion see [23].

Though outside the basis of this presentation, it is interesting to cite a quantum thermodynamic exorcism of the demon. It is shown that Maxwell's demon cannot accomplish his assignment because in any system in a thermodynamic equilibrium state the velocity of each and every molecule of a constituent is equal to zero [24].

## 5. A Promising Area for Investigation

Most of the energy sources that we use are based on fuels which upon combustion have an availability or exergy with respect to the environmental reservoir for use in land, sea, or air applications. Over the past about two and a half centuries tremendous progress has been made in improving the efficiency of energy use in each of these areas [25]. An outstanding example of this progress is the combined cycle of a natural gas turbine with a waste heat recovery steam power unit which has an overall thermal efficiency (ratio of overall power over the heating value of the gas) of about 63%, and a thermodynamic efficiency (ratio of overall power over the available energy after combustion) of about 90%. This kind of performance is graphically illustrated by the length of the dotted line between points 1 and 2 of Figure 2.

Next, consider the performance of the batteries that are used in electrically driven wrist watches, pacemakers, and other devices. In each of these applications, the time constant for self discharge is longer than the time constant for doing useful work, and consequently the available energy [10] is larger than the exergy for the given energy  $E$  and the same reservoir at temperature  $T$  used for the combined cycle, as shown in Figure 2. The question that intrigues me is the following: Is it possible to manufacture large scale energy sources which deliver their energy beginning from a state that is not a stable equilibrium state at an affordable cost and that require the same amount of primary energy as the engines that we use today? I do not know the answer to this question but I believe that it is worth looking into it.

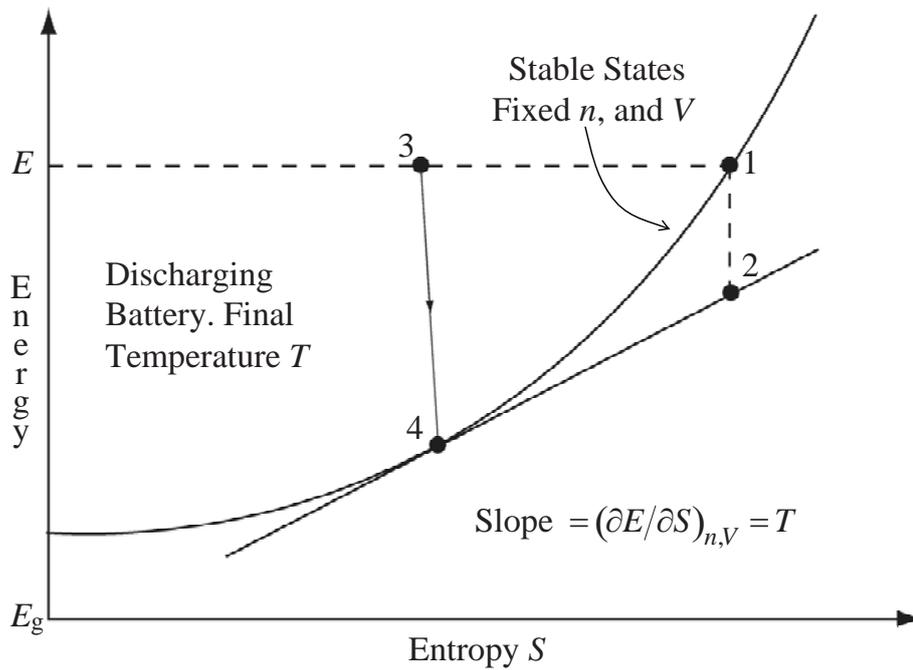


Figure 2. An illustration of a more effective use of an energy source that passes through states that are not stable equilibrium, such as the states between 3 and 4.

## 6. Conclusions

A nonstatistical theory of thermodynamics that applies to all systems (large or small), and to all states (thermodynamic equilibrium or any other kind encountered in mechanics) is briefly discussed. In this theory, entropy is shown to be a nonstatistical property of any system in any state, and the theory provides a more general physical (as opposed to statistical) regularization of natural phenomena than existed before, holds the promise of better understanding of the foundations of the subject, and more effective use of natural resources.

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