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Teaching Thermodynamics as a Science that Applies to any System (Large or Small) in any State (Stable or Not Stable Equilibrium)

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Abstract

The authors present a summary of their many years of experience in teaching at a graduate level a new exposition of thermodynamics. It is an exposition of the thermodynamics of a new non-statistical paradigm of physics and thermodynamics, which applies to both large and small systems (including one particle systems) in any state: thermodynamic (i.e. stable) equilibrium or not. It uses as its primitives the concepts of inertial mass, force, and time and introduces the laws of thermodynamics in the most unambiguous and general formulations found in the literature. Starting with a precise definition of system and of state followed by statements and corollaries of the laws of thermodynamics, the thermodynamic formalism is developed without circularity and ambiguity. Definitions of energy, generalized available energy, and entropy apply to all states and follow (instead of precede) statements of the laws of thermodynamics. All other property definitions as well as those for the work, heat, and other interactions, which a system may have with its surroundings, follow from these statements and corollaries as well. In addition, fundamental and characteristic relations as well as interrelations relating property changes in going from one neighboring stable equilibrium state to the next are defined and developed for the students, while multidimensional surfaces relating energy, entropy, external parameters (e.g., volume, surface area, electric field strength, magnetic field strength, etc.), and amounts of constituents for all states (stable or not stable equilibrium) are used to assist the student in visually picturing the states of a system and the processes the system undergoes.

Keywords: Thermodynamics, graduate-level teaching, non-statistical paradigm of physics and thermodynamics

1. Introduction

The science of thermodynamics has been developed and used since the 19th century to analyze various physical processes which occur in nature. Texts on classical or equilibrium thermodynamics such as some of the more recent ones written by Wark (1999); Black and Hartley (1997); Sonntag, Borgnakke, and Van Wylen (1998); Jones and Dugan (1996); Moran and Shapiro (2003); and Turns (2005), just to name a very few, deal with systems in states of stable (or thermodynamic) equilibrium or not. These expositions necessarily limit themselves to so-called macroscopic systems and any descriptions given in the classroom of the systems' underlying microscopic structure are used, for example, to relate temperature and pressure to the motions of the particles. This is consistent

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with the view initially promoted by Boltzmann in the 19th century that even at stable equilibrium, the particles are in motion and it is only their average velocity which is zero. This contrasts with the new exposition which makes no such connection since at stable equilibrium all the particles are motionless[1].

In order to deal with the underlying microscopic structure and its contribution to the behavior of macroscopic systems, the traditional approach has been to introduce statistical mechanical considerations. Texts which formally do so are those on statistical thermodynamics such as the ones written by Callen (1985); Lee, Sears, and Turcotte (1963); and Tien and Lienhard (1979), again to name a few. These texts describe systems in stable equilibrium with the goal of tying knowledge of a system's microscopic behavior into that at the macroscopic level. The microscopic behavior is described via quantum mechanical and semi-empirical inter-particle interaction models which when combined with the micro-canonical, canonical and grand canonical distributions resulting from the Maximum Entropy Principle lead to specific expressions for the fundamental relation

$$S = S\left(E, \vec{\beta}, \vec{n}\right) \qquad (1)$$

or some characteristic relation such as, for example, that for the energy E. From these relations all other thermodynamic properties can be derived by differentiation and algebraic manipulation. A statistical mechanical interpretation of these results is made by linking the entropy to the so-called thermodynamic probability of a macrostate and interpreting the increase of entropy in the system as a consequence of the natural trend of a system from a less probable to a more probable state. The thermodynamic probability is the number of microstates corresponding to a given macrostate.

In both of these approaches to thermodynamics, a clear demarcation exists between the microscopic world which is assumed to be reversible and where the laws of physics describe system states and behavior and the macroscopic world where the laws of thermodynamics are used to do the same. Thus, thermodynamics is viewed not as a discipline which describes all systems large and small (macroscopic or microscopic) in any state (stable or not stable equilibrium) but as a discipline limited exclusively to the macroscopic description of nature. Besides the obvious incompleteness this implies with regards to thermodynamics, there are also a number of real difficulties and paradoxes which arise from a statistical view or interpretation of nature such as that of Maxwell's demon's violation of the Second Law of thermodynamics[2] or how microscopic reversibility can lead to macroscopic irreversibility.

To address these issues, the new exposition of thermodynamics developed by Gyftopoulos and Beretta (1991, 2005) presents a contrasting view of nature in which thermodynamics applies to all macroscopic and microscopic systems in any state (stable or not stable equilibrium). This exposition seamlessly extends the formalism of thermodynamics down to the individual particle level and elegantly eliminates the paradoxes and many of the difficulties posed by the statistical paradigm. In doing so, the view of nature that it provides turns to one in which greater order is achieved the closer a system's state comes to stable equilibrium; entropy is no longer a statistically derived property of many particles but instead a fundamental or private property of matter in the same way that energy, momentum and inertial mass are; and irreversibilities can be graphically described in terms of the change in the quantum-theoretic shape of the constituents of a system as they respond to the internal and external forces to which they are subjected in a change of state.

The new exposition, i.e. one requiring no background whatsoever in quantum mechanics, appears in the text by Gyftopoulos and Beretta entitled *Thermodynamics: Foundation and Applications* (1991, 2005). It was this book which the authors chose some years ago and from which they have now taught for several years, using it as the basis for their first-level graduate thermodynamics courses. A description of the quantal exposition of the new non-statistical paradigm of physics and thermodynamics, which one of the authors chose for his second-level graduate thermodynamics course (von Spakovsky, 2005a), is outlined in an accompanying paper (von Spakovsky, 2006). However, it is the course on the new exposition of thermodynamics (Metghalchi, 2005; von Spakovsky, 2005b) which is outlined here in some detail in the following sections. Obviously, the entire course notes cannot be reproduced in a single paper so only the salient and distinguishing features which set this paradigm apart from all others are given below.

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[1] An exception to this is Brownian motion which is discussed in detail in Gyftopoulos (2005).

[2] Of the four hundred plus publications which claim to resolve the paradox of Maxwell's demon, only one does so without changing the problem as originally posed by Maxwell (Gyftopoulos, 1998).

2. The Thermodynamic Formalism

Unlike other courses based on all the texts which we have seen in which *system* is defined in an incomplete manner as simply the "subject of analysis" or "any region in space enclosed by a surface", the text by Gyftopoulos and Beretta (1991, 2005) provides a precise definition of *system* as a collection of constituents with the following specifications: the amounts of constituents $\vec{n} = \{n_1,...,n_r\}$, their type and range; parameters $\vec{\beta} = \{\beta_1,...,\beta_s\}$, their type and range; internal forces including internal reaction mechanisms; and internal constraints on changes in values of the n_i and the β_j. The β_j characterize external forces such as gravity, an electrostatic field, a magnetic field, or container walls, while internal forces and reaction mechanisms include chemical, nuclear, and molecular. Internal constraints include such things as internal partitions or the condition that all or some chemical reactions are inactive. Furthermore, partitioning of a system requires that the coordinates of each partition (i.e. subsystem) be separable from those of the other partitions and that the state of each partition be uncorrelated from that of the other partitions. It is assumed throughout Gyftopoulos and Beretta (1991, 2005) that *system* refers to *separable system*, and *state* to *uncorrelated state*.

Next, definitions of *property, state*, and *changes of state,* i.e. evolutions in time of state, follow. Two types of states exist: stable and not stable equilibrium. Of the latter, there are the non-equilibrium, metastable and unstable equilibrium, steady, and unsteady states. Certain time evolutions of state or processes are described by Newton's *equation of motion* or its quantum mechanical equivalent, the Schrödinger equation of motion. Other time evolutions, however, do not obey either of these equations such as those involving reversible heat transfer or those in which irreversibilities are present. An equation of motion which does is the Beretta equation (Beretta, Gyftopoulos, and Park, 1985). The most general and well-established features of all of these equations are captured by the First and Second Laws of thermodynamics which provide a powerful alternative procedure for analyzing the time-dependent phenomena of physical processes. Thus, we begin next with the most general and unambiguous statements of these two laws and their consequences, using as primitives space, time, and force or inertial mass.

2.1 The First Law of thermodynamics

The First Law of thermodynamics unique to Gyftopoulos and Beretta (1991, 2005) is

> "*Any two states of the 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.*"

Of course, for a fully rigorous treatment consistent with special relativity, this statement of the first law would have to be modified by replacing the quantity $Mg(z_1 - z_2)$ with $Mc^2(exp(gz_1/c^2) - exp(gz_2/c^2))$ where c is the speed of light in a vacuum and M is the mass of the weight at $z = 0$. For purposes of the course the authors each teach, however, the statement above is more than sufficient.

What makes this statement so general and encompassing of all other statements of the First Law is that it applies to any system in any state undergoing any type of process and only requires as primitives M, g, and z. The implication of this statement of the First Law is the existence of a property called the energy E, i.e. the energy of a system A in some state A_1 is defined as

$$E_1 = E_o - Mg(z_1 - z_o) \tag{2}$$

where as is the case for all thermo-physical properties, the energy must be defined with respect to some reference energy E_o, M is the inertial mass of the weight, and z_1 and z_o are the heights of the weight when the system is in state A_1 and A_o, respectively. It can further be shown as first and second corollaries or theorems of the First Law that the energy is additive and conserved. This last is easily proven by showing that any change of state of a system can always be considered as part of a zero-net-effect process of a composite of the system and its environment. Both of these theorems then lead to a third, namely, that of an energy balance expressed in general terms on a rate basis by

$$\frac{dE}{dt} = \dot{E}_t + \dot{E}_p \tag{3}$$

where $\dot{E}_t$ is the net rate of energy transferred to the system via interactions which a system has with its environment or other systems, while $\dot{E}_p$ is the net rate of energy produced. This term is usually zero unless nuclear reactions are active during the process that the system undergoes. Of course, on a non-rate basis this balance is written as:

$$E_2 - E_1 = E_t + E_p \qquad (4)$$

The energy interactions which a system may undergo are classified into two principal types: pure energy transfers which define the concept of *work (W)*, i.e. the only extensive property involved in the transfer is energy, and all other interactions classified as non-work where the transfer involves not only energy but other extensive properties as well. However, since we have as yet to define these other extensive quantities, we leave further discussion of these to later. We instead now turn our focus to the Second Law of thermodynamics.

2.2 The Second Law of thermodynamics

Again as before, unique to Gyftopoulos and Beretta (1991, 2005), is the following statement of the Second Law of thermodynamics:

> *"Among all the states of a system with a given value of the energy E and given values of the amounts of constituents $\vec{n}$ and the parameters $\vec{\beta}$, there exists one and only one stable equilibrium state."*

Notice that this statement is completely general[3] and only requires the First Law which establishes our property E and our precise definition of state and system which establishes $\vec{n}$ and $\vec{\beta}$. No other extensive properties, definitions of cycles and types of interactions, or any other concept are required. Furthermore, it can be shown that all other statements of the Second Law such as those, for example, by Kelvin-Planck, Clausius, and Caratheodory follow as a special consequence of the general statements of the laws of thermodynamics given above. Another important aspect is that from this statement two very powerful corollaries follow, i.e. the Maximum Entropy Principle and the Minimum Energy Principle. However, to establish these corollaries one must first define the extensive property called the *entropy* which itself must be preceded by defining two other extensive properties called the *generalized adiabatic availability* and the *generalized available energy*.

2.3 Generalized adiabatic availability and available energy

The *adiabatic availability* Ψ is defined as the maximum amount of work that can be done by a system in a work interaction while keeping the amount of constituents $\vec{n}$ and parameters $\vec{\beta}$ fixed. It becomes the *generalized adiabatic availability* when both $\vec{n}$ and $\vec{\beta}$ are allowed to vary. In this case, Ψ is either the maximum or minimum amount of work produced or required. To produce the maximum amount of work, the system undergoes a *reversible process*[4] in which no non-work interactions are present (hence the term *adiabatic*[5]) and the final state is in stable equilibrium. One can prove that the *adiabatic availability* is always greater than or equal to zero. It is zero when the system's initial state is one of stable equilibrium and positive when it is not. In general, when Ψ is simply the *adiabatic availability*

$$\Psi \geq W \geq 0 \qquad (5)$$

Furthermore, one can easily prove that this extensive property is not additive by taking two systems A and B, both in a state of stable equilibrium, and combining them into a composite system C whose state is not necessarily a state of stable equilibrium. Clearly, based on our definition above, Ψ_A and Ψ_B are zero while Ψ_C is not necessarily. Therefore, $\Psi_C \neq \Psi_A + \Psi_B$. Also, note that this extensive property is not limited to states only in a state of stable equilibrium. Thus, it is completely general and applies to any system (large or small) in any state (stable or not stable equilibrium). However, though of interest, this extensive property is not particularly useful in analyzing systems since no balances can be formed of this quantity. We, thus, turn to the definition of a general extensive property for which such balances exist, namely the *generalized available energy* Ω.

Ω is defined as the optimum (maximum or minimum) amount of work that a composite of a system and its environment can produce or require while allowing the amount of constituents $\vec{n}$ and parameters $\vec{\beta}$ to vary. When $\vec{n}$ and $\vec{\beta}$ remain fixed, Ω reduces to the *available energy*. Again as before, the process which both the system and its environment undergo must be reversible and the final state of the composite of the system and its environment is one of not only stable equilibrium but of mutual stable equilibrium with each other. Of course, Ω is always greater than or equal to zero when Ω is simply the *available energy*. When it is the *generalized available energy*, Ω can be

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[3] The Second Law statement adopted by the MIT school of thermodynamics must be traced to the pioneering work by Hatsopoulos and Keenan (1965).

[4] A *reversible process* is one in which the system and its environment can be restored to their respective initial states.

[5] Note that this definition of *adiabatic* encompasses the much narrower definition found in most other texts in which *adiabatic* is defined with respect to only one type of non-work interaction.

both negative, positive, or zero[6]. Ω is zero when the system is in a state of mutual stable equilibrium with its environment.

It is also true and can easily be shown that the absolute value of Ω is always greater than or equal to that of Ψ, i.e.

$$|\Omega| \geq |\Psi| \qquad (6)$$

Furthermore, once again note that Ω, as was the case for Ψ, is completely general and applies to any system (large or small) in any state (stable or not stable equilibrium). In addition, the proof that Ω is additive is straightforward as is the fact that it is a *non-conserved* extensive property of the system with respect to a given environment or reservoir. Thus, in analyzing the system, one can write balances of Ω such that

$$\frac{d\Omega}{dt} = \dot{\Omega}_t + \dot{\Omega}_d \qquad (7)$$

where

$$\dot{\Omega}_d \leq 0 \qquad (7a)$$

and where the rate of destruction term $\dot{\Omega}_d$ is positive for any *irreversible process*[7] and $\dot{\Omega}_t$ is the net rate of transfer to the system of available energy due to the different types of interactions (work and non-work) which the system undergoes.

It is this extensive property Ω, which applies to all systems in any state that can now be used to define an extensive property called the *entropy S* which itself will apply to all systems in any state.

2.4 The entropy of thermodynamics

The *entropy S* of thermodynamics can now be defined in completely general terms as

$$S = S_o + \frac{1}{C_R}\left[(E - E_o) - (\Omega - \Omega_o)\right] \qquad (8)$$

where S, as the energy earlier, is defined with respect to some reference value S_o, the subscript o refers to the reference environment or reservoir, and C_R is a constant that can be shown to be an intensive property of the environment or reservoir[8].

Of course, although it is obvious from this expression that since S is a function of E and Ω only that S must also apply to any system (large or small) in any state (stable or not stable equilibrium), the question arises, “is S a property of the system only or of the system and the environment or reservoir?”. Based on the expression above, it would appear at first glance that the latter is true. However, it can be proven with some effort (see the elegant proof given on pp. 108-112 of Gyftopoulos and Beretta (1991, 2005)) that S is an extensive property of the system *only*. Furthermore, it can be shown that this definition of the *entropy* is consistent with the quantum mechanical based expression which arises from the new non-statistical paradigm developed by Gyftopoulos and his co-workers and that this entropy is the only one sufficiently general and coherent to be called the “entropy of thermodynamics”. A proof of this is given in Gyftopoulos and Çubukçu (1997). This *entropy*, unlike the statistically based ones which arise out of the statistical paradigm of physics and thermodynamics, is in fact a fundamental or private property of matter in the same way that energy, inertial mass, and momentum are. The implication of this revolutionary view of *entropy* is that the *entropy creation* (or *production*) $\dot{S}_p$ as it appears in the following balance for the *entropy*:

$$\frac{dS}{dt} = \dot{S}_t + \dot{S}_p \qquad (9)$$

where

$$\dot{S}_p \geq 0 \qquad (9a)$$

is due to the change in the quantum-theoretic shape of the constituents of a system as they respond to the internal and external forces acting upon them (Gyftopoulos and von Spakovsky, 2003). Furthermore, contrary to the view originating with Boltzmann and Maxwell and held since the 19th century, *entropy* is established as a measure of “order” and not “disorder” (Gyftopoulos,1998; Gyftopoulos and Çubukçu, 1997) which in turn fundamentally changes how one views nature.

Having now established a number of important extensive properties, we can proceed to the next stage in our development of the thermodynamic formalism, namely, the graphical

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[6] When the *generalized available energy Ω* is positive, it represents the maximum work that the composite can produce as the system and the environment come to mutual stable equilibrium with each other; and when negative, it is the minimum amount of work required to bring the system and its environment into mutual stable equilibrium with each other (Rezac and Metghalchi, 2004; Ugarte and Metghalchi, 2005).

[7] An *irreversible process* is one in which the system and its environment cannot be restored to their respective initial states.

[8] In fact, it can be proven that C_R is the thermodynamic temperature of the reference environment or reservoir (Gyftopoulos and Beretta, 1991, 2005).

presentation of a number of other important concepts, i.e. intensive properties, property interrelations, the generality of Ψ and Ω, the *Maximum Entropy* and *Minimum Energy Principles*, work and non-work interactions, etc.

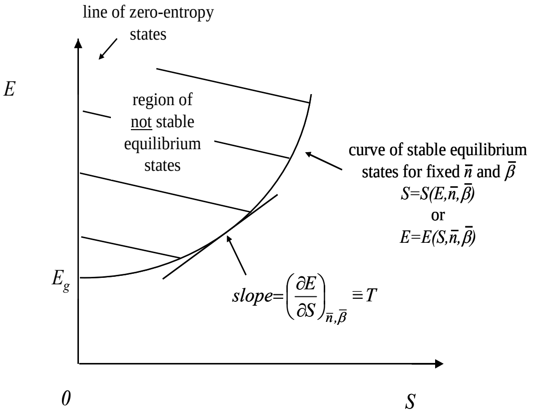

Figure 1. A two-dimensional slice of a hyper-surface of E versus S for fixed $\vec{\beta}$ and $\vec{n}$ depicting the various domains of physics and thermodynamics.

2.5 Hyper-surfaces of *E, S,* $\vec{\beta}$, and $\vec{n}$

A graphical description of the general science of thermodynamics which emerges from the discussions of the new exposition of thermodynamics given in the previous sections appears in *Figure 1*. The figure is a representation of a two-dimensional slice in the *E-S* plane of a *E-S-* $\vec{\beta}$ - $\vec{n}$ hyper-surface of stable equilibrium states. The parabolic curve given by the characteristic function

$$E = E\left(S,\vec{\beta},\vec{n}\right) \tag{10}$$

or by the fundamental relation, equation (1), consists of all possible stable equilibrium states for a given system at fixed composition $\vec{n}$ and fixed parameters $\vec{\beta}$. The slope at each point on this curve is defined as the thermodynamic temperature, i.e.

$$T \equiv \left.\frac{\partial E}{\partial S}\right)_{\vec{\beta},\vec{n}} \tag{11}$$

while the slopes for other two-dimensional slices of this hyper-surface result in the generalized forces f_j conjugated to the parameters β_j and in the total potentials μ_i linked with the constituent amounts n_i, i.e.

$$f_j \equiv \left.\frac{\partial E}{\partial \beta_j}\right)_{\vec{\beta}(i\neq j),\vec{n}} \tag{12}$$

$$\mu_i \equiv \left.\frac{\partial E}{\partial n_i}\right)_{\vec{\beta},\vec{n}(j\neq i)} \tag{13}$$

where when β_j is the volume V, f_j is the negative of the thermodynamic pressure P, while μ_i reduces to the chemical potential for, for example, simple systems, i.e. when $\vec{\beta} = \{V\}$ Furthermore, a first-order Taylor series expansion, representing infinitesimal changes in the extensive properties *E, S,* $\vec{\beta}$, and $\vec{n}$ along the hyper-surface of stable equilibrium states, results in the *differential energy relation*, i.e. the well-known Gibbs relation, given by

$$dE = TdS + \sum_{i=1}^{r}\mu_i dn_i + \sum_{j=1}^{s} f_j d\beta_j \tag{14}$$

Equation (13) in effect constrains how changes in the extensive properties *E, S,* $\vec{\beta}$, and $\vec{n}$ can be made in moving from one neighboring stable equilibrium state to another on the hyper-surface.

For systems with $\vec{\beta} = \{V\}$, Equation (14) reduces to

$$dU = TdS - PdV + \sum_{i=1}^{r}\mu_i dn_i \tag{15}$$

where *E* has been replaced by *U* the internal energy. From Equation (14), one can derive a set of *Maxwell relations* and for a simple system[9] the *Euler relation* as well as the *Gibbs-Duhem* relation. The latter is given by

$$SdT - VdP + \sum_{i=1}^{r} n_i d\mu_i = 0 \tag{16}$$

and constrains in a fashion similar to Equation (13) how changes in the intensive properties *T*, *P*, and μ_i can be made in moving from one neighboring stable equilibrium state to another on the hyper-surface.

2.6 The validity of Ψ and Ω for all states

From these relations and characteristic functions all thermodynamic (thermo-physical) properties can be derived and equations of state developed for any system in a state of stable equilibrium. However, it is not just the hyper-surface of stable equilibrium states which provides useful information but the space between the surface and the vertical axes as well (e.g., in two-dimensions, the hatched area between the curve and vertical axis in *Figure 1* and the space between the surface and the left-hand face of the box in *Figure 2*). For example, the generality of the *generalized adiabatic*

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[9] A simple system is defined as one for which $\vec{\beta} = \{V\}$, partitioning of the system when in a stable equilibrium state has negligible effect, and the switching on and off of internal mechanisms causes negligible changes in the instantaneous values of *E, S,* $\vec{\beta}$, and $\vec{n}$.

availability and *available energy* concepts as defined by Gyftopoulos and Beretta (1991, 2005) can be clearly seen in *Figure 2* where, for example, some system A in a not stable equilibrium state A_1 has values of Ψ_1 and Ω_1 given by the difference in energy between states A_1 and A_{S_1} and between state A_1 and the point "a", respectively, where state A_{S_1} and point "a" are identified by the value of the entropy of the given state A_1 and the given value of the final volume. In contrast, if the same system with the same *energy* E_1 is in a state of stable equilibrium A_{E_1}, the *generalized available energy* Ω_{E_1} (or in this case the *exergy*) is given by the difference in energy between A_{E_1} and the point "b". Cleary, $\Omega_1 > \Omega_{E_1}$, pointing to the definite advantage that the system derives from being in a not stable as opposed to stable equilibrium state with energy E_1. Furthermore, as should be evident from the comparison just made, the *generalized available energy* is a more general concept than that of the *exergy* which derives from classical thermodynamics since the former is not limited to states of stable equilibrium, i.e. the *exergy* is a special case of the *generalized available energy*.

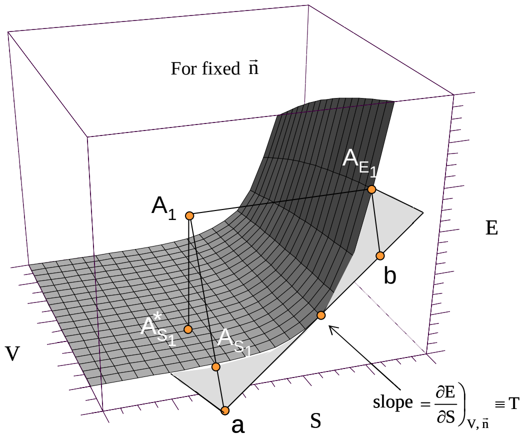

Figure 2. Energy versus entropy versus volume for a simple system of fixed composition.

2.7 The Maximum Entropy and Minimum Energy Principles

Now, again looking at *Figure 2*, if system A is isolated, its state at A_1 is a non-equilibrium state which will spontaneously change until the state of the system reaches that of stable equilibrium at A_{E_1}. This process helps define what is known as the *Maximum Entropy Principle* which consists of maximizing the entropy of a system while keeping E, $\vec{\beta}$, and $\vec{n}$ fixed so that state A_1 evolves into A_{E_1}. In a similar vein, the *Minimum Energy Principle* is based on a reversible work process which system A in state A_1 (of course, no longer isolated) undergoes in order to reach state $A^*_{S_1}$. In this case, the energy is minimized holding S, $\vec{\beta}$, and $\vec{n}$ fixed. Both principles are used routinely in the quantal exposition of the new non-statistical paradigm of physics and thermodynamics to develop canonical and grand canonical distributions which are then used in the determination of expressions for the thermodynamic properties of, for example, ideal and real gases. A discussion of this appears in von Spakovsky (2006).

2.8 Perpetual motion machines of the second kind

Figures 1 and *2* can also be used to easily illustrate the impossibility of a perpetual motion machine of the second kind (PMM2). For example, if system A is in state A_{E_1} or A_{S_1} or any other state of stable equilibrium, it is impossible to extract energy from the system in a work interaction without net changes in $\vec{\beta}$ and $\vec{n}$ because no state of lower energy exists with a value of S greater than or equal to that of the system in its initial state of stable equilibrium. The need for constructing an elaborate set of cycles and reservoirs to prove the impossibility of the PMM2 as is done in most texts on classical thermodynamics is completely and easily avoided here.

2.9 Work and non-work interactions

As to both work and non-work interactions, those for work, heat, bulk flow, and diffusion are listed in TABLE I. The first of these transfers energy and available energy but no entropy and mass while a heat interaction, which involves a system-surroundings interface temperature T_Q (Gyftopoulos and Beretta, 1991, 2005), transfers energy, available energy, and entropy but no mass. The interface temperature T_Q in fact helps to clearly define what a heat interaction is and to distinguish this type of interaction from other non-work interactions.

Other non-work interactions include those for bulk flow and diffusion where not only energy, generalized available energy, and entropy are transferred but mass as well. Furthermore, the state of the mass transferred during a bulk flow interaction is that of a simple type of *non-equilibrium* state that can be characterized by a limited set[10] of thermodynamic properties S, E, $\vec{\beta}$, and $\vec{n}$ which describe the stable equilibrium state of a simple

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[10] In general, a not stable equilibrium state must be described by a much larger set of properties than the limited set specified here.

system[11] and a set of mechanical properties ξ and z.

TABLE I. TYPES OF SYSTEM INTERACTIONS AND QUANTITIES TRANSFERRED.

Trans-ferred Quan-tity	**Interaction**			
	Work	**Heat**	**Bulk Flow**$^{(a)}$	**Diffusion**$^{(b)}$
Energy	W	Q	$\left(h+\frac{\xi^2}{2}+gz\right)n_t$	E_t
Avail-able Energy	W	$\left(1-\frac{T_o}{T_Q}\right)Q$	$\left(h-T_o s-\mu_o \quad \frac{\xi^2}{2}+gz\right)n_t$	$\left(1-\frac{T_o}{T_D}\right)\left(E_t-\mu_D n_t\right)$
Entropy	0	$\frac{Q}{T_Q}$	sn_t	$\frac{E_t-\mu_D n_t}{T_D}$
Mass	0	0	n_t	n_t

(a) The specific enthalpy and entropy are those associated with the stable equilibrium state portion of the bulk flow state, while the speed and elevation are the mechanical properties of the bulk flow state (Gyftopoulos and Beretta, 1991, 2005)

(b) In the limit as n_t goes to zero, the diffusion interaction becomes a heat interaction (Gyftopoulos, Flik, and Beretta, 1992).

Since the bulk flow state is a non-equilibrium state, the intensive properties T, P, and μ_i and, as a consequence, H, A, and G, *cannot* be defined for the bulk flow state as such even though in practice one typically refers to these properties as those of the bulk flow state. They can, however, be defined for the stable equilibrium state of a simple system that has an internal energy U described by the characteristic function

$$U = U\left(S, \vec{\beta}, \vec{n}\right) \tag{17}$$

where for a simple system $\vec{\beta} = \{V\}$. As a consequence, the energy E of the bulk flow state can be expressed by

$$E = U\left(S, V, \vec{n}\right) + \frac{n\xi^2}{2} + ngz \tag{18}$$

Thus, for example, if state A_1 in *Figure 3* is a bulk flow state, one can characterize its energy using equation (17) even though it does not fall on the hyper-surface of stable equilibrium states. Nonetheless, it should be clear that bulk flow states form a special and restrictive class of non-equilibrium states since *not* all non-equilibrium states satisfy the requirement that $E - m\xi^2/2 - mgz$ be an energy related to S, V, and $\vec{n}$ in accordance with the *State Principle* (Gyftopoulos and Beretta, 1991, 2005).

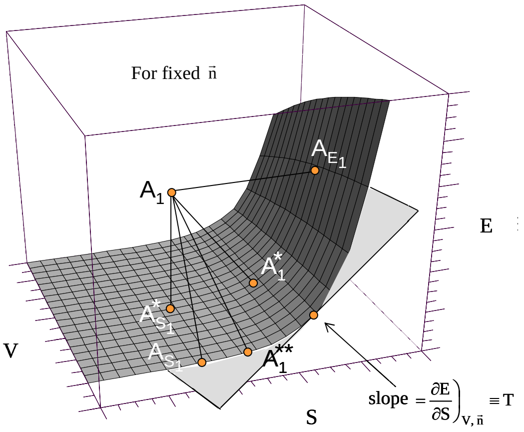

Figure 3. Example of a hyper-surface of E, S, and V for a simple system of fixed $\vec{n}$ used to graphically describe the types of interactions that the system can undergo.

Finally, the diffusion interaction is another type of non-work interaction that can be clearly distinguished from those for bulk flow and heat. The quantities transferred with this type of interaction are listed in TABLE I. Since it is an interaction, it is *not* a property of the system and is, thus, not contained by the system. It is a mode of transfer which transfers energy, entropy, and mass in such a way that the following relationship holds (Gyftopoulos, Flik, and Beretta, 1992):

$$S_t = \frac{E_t - \mu_D n_t}{T_D} \tag{19}$$

where T_D and μ_D are the diffusion temperature and total potential, respectively, as defined in Gyftopoulos, Flik, and Beretta (1992). In the limit, as n_t goes to zero, the diffusion interaction becomes a heat interaction. In order to describe the various types of interactions which a system

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[11] A *simple system* is defined as having volume as the only parameter and satisfying the following two additional requirements:

i) If the system in any of its stable equilibrium states is partitioned into subsystems all of which are in mutual stable equilibrium with each other, the effects of the partitioning is negligible;

ii) If the system is in any of its stable equilibrium states, the instantaneous turning on or off of any internal reaction mechanisms results in negligible instantaneous changes in the values of E, S, V, and $\vec{n}$.

undergoes, it can be quite useful to picture them graphically. For example, referring to *Figure 3* once more, the process from A_1-A_{E_1} might be that of an isolated simply system (i.e. there are no interactions) which initially is in a state of non-equilibrium and spontaneously changes its state to a state at stable equilibrium, generating entropy in the process. The process A_1- $A^*_{S_1}$ is an isentropic process of for example, a simple system as is the process from A_1-A_{S_1}, the difference being that the first occurs at constant volume while the second does not. In either case, the process either occurs reversibly and adiabatically, producing work in the process (i.e. only a work interaction is present) or irreversibly and non-adiabatically with, for example, the system undergoing both work and heat interactions. The processes A_1- A_1^* and A_1- A_1^{**} are at first glance examples of irreversible processes at constant and variable volume, respectively, since the entropy increases but they could just as well be reversible with both work and non-work interactions taking place. More details can be gleaned from these types of diagrams specific to the systems, states, processes, and interactions present, helping the student to graphically picture a particular application. They are used extensively by both authors in their respective courses both in 2D and 3D in a manner similar to that of the stable equilibrium diagrams of classical thermodynamics (e.g., the Mollier diagram) except that the former include all states, not just those of stable equilibrium.

3. Conclusions

It has often been said that *thermodynamics* is a particularly difficult science to learn but more importantly to understand. The great physicist Arnold Sommerfeld asked once why he had never written a book on thermodynamics replied that

> *"The first time I studied the subject I thought I understood it except for a few minor points. The second time, I thought I did not understand it except for a few minor points. The third time, I knew I did not understand it, but it did not matter, since I could use it effectively."*

It is overcoming this third point of failing to clearly understand, which motivated the authors to search for a clearer understanding of this science. This in turn led us both to independently be intrigued by the new exposition of thermodynamics outlined in this paper, a paradigm that presents thermodynamics as a broad and general science not limited only to certain types of systems (large) nor to certain types of states (stable equilibrium). It is this science, which we have both taught to our graduate students over the last several years and which we believe has provided them with a much clearer and broader understanding of this science. In turn, we hope that what we have written will also be sufficiently intriguing to spark others to take a deeper look at this new and general exposition of thermodynamics.

Nomenclature

c	speed of light
E	energy
f	generalized force
g	acceleration of gravity
h	specific enthalpy
M	inertial mass of a weight
n	amount of constituent
S	entropy
P	pressure
T	temperature
U	energy of a system with volume as the only parameter
V	volume
W	work or work interaction
z	elevation in a gravity field

Greek Letters

β	parameter
μ	total or chemical potential
Ω	generalized available energy
Ψ	generalized adiabatic availability
ξ	speed

Subscripts

D	diffusion
d	destruction
o	reference state or environment or reservoir
p	production
Q	heat interaction
R	reference environment or reservoir
t	transfer or interaction

Superscripts

$\cdot$	indicates a rate quantity

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