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Teaching the Quantal Exposition of the Unified Quantum Theory of Mechanics and Thermodynamics

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Abstract

The author presents his experience in teaching at a graduate level the *quantal* exposition of a new non-statistically based paradigm of physics and thermodynamics. This paradigm, called the *Unified Quantum Theory of Mechanics and Thermodynamics,* applies to all systems large or small (including one particle systems) either in a state of thermodynamic (i.e. stable) equilibrium or not in a state of thermodynamic equilibrium. It uses as its primitives 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. In this *quantal* exposition of the new paradigm, a brief review of the formalism of thermodynamics as a general science *not* limited to stable equilibrium and large (macroscopic) systems as well as a very brief summary of the three prevalent formalisms in classical physics are presented followed by a presentation and development of solutions for a number of elementary problems in quantum physics (e.g., a particle in a box, a harmonic oscillator, a rigid rotor, etc.). These solutions and the maximum entropy principle are then used in a constrained optimization to develop the canonical and grand canonical distributions for Fermi-Dirac and Bose-Einstein types of particles, i.e. for fermions and bosons. This is done *without* the use of analogies between statistical and thermodynamic results and *without* additional hypotheses such as the ergodic hypothesis of statistical mechanics. These distributions are then employed under various assumptions (i.e. the Boltzmann, constant-potential, point-particle, and continuous eigenvalue-spectrum approximations) to derive the corresponding thermodynamic property expressions for perfect, semi-perfect (ideal), and Sommerfeld gases as well as for mixtures of ionized and dissociated gases. In a similar fashion but with a change from a single- to a multi-particle partition function and with the addition of various inter-particle potentials for two-particle interactions (e.g., the Lennard-Jones potential, the square-well potential, etc.), expressions for the thermodynamic properties of dense gases are developed and presented.

Keywords: Quantum mechanics, thermodynamics, graduate level teaching, non-statistical paradigm of physics and thermodynamics, unified quantum theory of mechanics and thermodynamics

1. Introduction

This paper presents the author's experience in teaching at a graduate level a new non-statistically based paradigm of physics and thermodynamics called the *Unified Quantum Theory of Mechanics and Thermodynamics* (Hatsopoulos and Gyftopoulos, 1976, 1979; Beretta, Gyftopoulos, and Park, 1985; Gyftopoulos and Beretta, 1991, 2005;

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Gyftopoulos and Çubukçu, 1997; Gyftopoulos and von Spakovsky, 2003, 2004; Beretta and Gyftopoulos, 2004). Having taught both the *non-quantal* (Gyftopoulos and Beretta, 1991, 2005; von Spakovsky, 2005; Metghalchi, 2005; von Spakovsky and Metghalchi, 2006) and *quantal* (Hatsopoulos and Gyftopoulos, 1976, 1979; Beretta, Gyftopoulos, and Park, 1985; Gyftopoulos and Çubukçu, 1997; Gyftopoulos and von Spakovsky, 2003, 2004; Beretta and Gyftopoulos, 2004; von Spakovsky, 2006) expositions of this theory over the last several years, it was suggested by a number of my colleagues that a paper on the *quantal* exposition would be of interest since what is generally taught today is the statistical mechanical based paradigm of statistical thermodynamics which has been the dominant paradigm since the 19th century. An accompanying paper co-authored with my colleague Hameed Metghalchi does the same for the *non-quantal* exposition (von Spakovsky and Metghalchi, 2006).

Whichever exposition of the Unified Theory is taught, the paradigm itself applies to any system large or small (including one particle systems) either in a state of thermodynamic (i.e. stable) equilibrium or not. It uses as its primitives 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 uniquely precise definition of system and of state followed by statements and corollaries of the laws of thermodynamics, this thermodynamic formalism avoids both circularities and ambiguities. In the *quantal* exposition presented here, the course taught is outlined beginning with a brief summary of the formalism of thermodynamics and the formalisms and failures of classical physics followed by solutions for a number of elementary problems in quantum physics (e.g., a particle in a box, an harmonic oscillator, a rigid rotor, etc.), which, along with the maximum entropy principle, are used in a constrained optimization to develop the canonical and grand canonical distributions for Fermi-Dirac and Bose-Einstein types of particles, i.e. for fermions and bosons. This is done _without_ the use of analogies between statistical and thermodynamic results and _without_ additional hypotheses such as the ergodic hypothesis of statistical mechanics. These distributions are then employed under various assumptions (i.e. the Boltzmann, constant-potential, point-particle, and continuous eigenvalue-spectrum approximations) to derive the corresponding thermodynamic property expressions for perfect, ideal, and Sommerfeld gases as well as for mixtures of ionized and dissociated gases. In a similar fashion but with a change from a single- to a multi-particle partition function and with the addition of various inter-particle potentials for two-particle interactions (e.g., the Lennard-Jones potential, the square-well potential, etc.), expressions for the thermodynamic properties for dense gases are developed and then presented. However, before beginning with this exposé, a brief history of the significant contributions made with regards to the unified theory is made.

2. Brief History of the Unified Theory

The first presentation of this new paradigm of physics and thermodynamics is given by Hatsopoulos and Gyftopoulos (1976) in a series of four papers. Called the *Unified Quantum Theory of Mechanics and Thermodynamics*, the theory unifies these two disciplines of science and resolves a number of the dilemmas and paradoxes that have plagued generations of physicists and thermodynamicists in their attempts to rationalize the relationship between mechanics and thermodynamics. This work is a landmark development, which indeed fits the definition of a radical or revolutionary change in the way we think and conceive of thermodynamics and physics. As described in Thomas Kuhn's book *The Structure of Scientific Revolutions* (1970), such a change is what has marked the shift throughout history from one major paradigm to another, e.g., the shift from classical to quantum mechanics or to general and special relativity or from the Ptolemaic theory to the heliocentric theory. This work represents the basis on which Gyftopoulos and his colleagues have continued over the last three decades to develop this unified theory, which encompasses without modification all systems (both large and small) and all states (both thermodynamic or stable equilibrium and not stable equilibrium). The foundations laid here lead next to the discovery of a completely new equation of motion.

Having observed that Newton's and Schrödinger's equations of motion and the latter's equivalent the von Neumann equation are correct but incomplete, Beretta (Beretta, Gyftopoulos, and Park (1985)) proceeded to develop in the context of the unified theory a new and much more comprehensive equation of motion. To put this in perspective, the Schrödinger equation, for example, only describes a special case of processes, which are reversible and adiabatic and describe the evolution of a system from one mechanical state to another. Such processes are called unitary in quantum mechanics. However, not all reversible processes are unitary. For example, the transfer of energy from one system at a high temperature to another at a low temperature in a reversible heat interaction represents a process fundamental to thermodynamics but one, which is not unitary and, thus, not describable by the Schrödinger equation. Furthermore, von Neumann's equation for unitary transformations of the density operator in time is also not sufficiently general to encompass this type of reversible process, i.e. non-unitary process, since his density operator is both a statistical average of wave functions or projectors and each statistical weight is independent of time. In addition, neither the Newton, Schrödinger, nor von Neumann equations of motion are able to describe a whole class of processes which one encounters in thermodynamics, namely irreversible processes.

In contrast to these equations, the equation of motion developed by Beretta encompasses these other equations as special cases and is able to predict the evolution in time of the state of a system not only for unitary reversible processes but for irreversible processes as well. None of the other equations of motion proposed over the last century are able to do this and, thus, the Beretta equation of motion is not only the most general but is as well an illustration of the unification which this theory brings to mechanics and thermodynamics since it is able to predict the evolution in time of a system's state be it mechanical or thermodynamic. In fact, the Beretta equation is equivalent to using the laws of thermodynamics with the factor of time introduced to predict not only the evolution of a state but the time it takes to go from one state to the next.

In 1991, Gyftopoulos and Beretta published their *non-quantal* exposition (a 2nd edition has since been released, 2005) of Thermodynamics that defines all concepts and results rigorously and completely and without circular or tautological arguments. Though the intellectual basis for this exposition is the Unified Theory, the presentation given in their book is done <u>without</u> reference to quantum-theoretic concepts, postulates and theorems and can, thus, be studied without knowledge of quantum theory. It is, therefore, a beautiful introduction into the generality of thermodynamics and its applicability to all systems whether microscopic or macroscopic or in a state of stable equilibrium or a state of not stable equilibrium. This contrasts with all other presentations of thermodynamics, which assume, as classical thermodynamics does, that thermodynamics stops (using the terminology of statistical mechanics) at the boundary between the macroscopic and the microscopic and that thermodynamic concepts such as entropy apply only to states in stable equilibrium and are not fundamental to matter in the same way that mass, energy and momentum are.

In a 1997 landmark article, Gyftopoulos and Çubukçu posed and then conclusively answered the question: are all the numerous expressions for entropy, which proliferate the literature, acceptable as the entropy of thermodynamics? Gyftopoulos and Çubukçu answer this question with an emphatic "no" by establishing a set of eight criteria, which the entropy of thermodynamics must meet. These criteria are based on the Unified Theory and are used to screen the most likely candidate expressions, namely, the quantum expressions by Daróczy (1970), by Hartley (1928), by Rényi (1966), and by von Neumann (1929) as well as the infinite norm entropy expression and the one developed by Hatsopoulos and Gyftopoulos (1976)[1]. Expressions for entropy based on temperature and heat (typical of classical or equilibrium thermodynamics) are excluded because they only apply to stable equilibrium states while those which come from statistical mechanics are not acceptable because they are based on statistical (i.e. subjective) as opposed to quantal (i.e. inherent) probabilities and the entropy which results is, therefore, not a fundamental property of matter. Furthermore, expressions, which come from statistical quantum mechanics and depend on variables other than the eigenvalues of the density operator, are also excluded because they fail the criterion that entropy must be invariant or increase. Thus, of the expressions listed above, only the one, which comes from the Unified Theory, satisfies all eight criteria. All others fail at least one and most more than one.

Thus, with this important work, the entropy of thermodynamics is established as a non-statistical property of matter in any state, not just a stable equilibrium state. 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 <u>not</u> "disorder" which in turn fundamentally changes how one views nature. These conclusions lead to the idea that entropy creation is a measure of how the constituents of a system be it large or small change or evolve in response to the internal and external forces acting upon them and that this change can be graphically seen as the change in the quantum-theoretic shape of the constituents. The latter is the next important contribution (Gyftopoulos and von Spakovsky, 2003), which is discussed.

In Gyftopoulos and von Spakovsky (2003), the authors make a novel and potentially important contribution to the field of

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[1] The original proof by Hatsopoulos and Gyftopoulos (1976) is completed and generalized in Gyftopoulos and Çubukçu (1997).

thermodynamics. Viewing entropy as a fundamental property of matter (like mass or momentum or energy) independent of statistical considerations, the authors assert that entropy can be characterized by shape, and that the concept applies to individual atoms and molecules, not just to macroscopic ensembles. The aspect stressed in this paper is the observation that the shape of the probability density function is rippled and unstable for not stable equilibrium states and is smooth and stable for stable equilibrium.

These are remarkable assertions, and the first presentation of quantum theoretic shapes (in terms of spatial coordinates) within the context of the Unified Theory. Its originality lies beyond the fact that this is a novel exposition of quantum theoretic shapes, since spatial distributions or shapes have already been treated to a degree within the framework of quantum mechanics. Instead, its originality lies in the fact that since the Unified Theory encompasses quantum mechanics as a special case, there is a need for generalizing the concept of spatial shapes to thermodynamics as a whole. This paper clearly fills that important gap. To this end, this work accomplishes a great task in explaining a number of the features of the Unified Theory.

Finally, in the latest contribution to this new theory, Beretta and Gyftopoulos (2004) make a significant contribution to the literature by developing analytical expressions for chemical affinities, reaction rates, and entropy generation rates as functions of the reaction coordinates for states near chemical equilibrium. The conditions for chemical equilibrium as a system proceeds through non-equilibrium states towards chemical equilibrium are established in terms of energy, volume, and composition or temperature, pressure, and composition. The model developed is valid for the homogeneous states of reactors and provides the conceptual basis for the so-called “local-equilibrium” assumption on which the continuum fluid dynamics’ treatment of non-homogeneous states rests. Of even greater import is Gyftopoulos’ and Beretta’s *non-statistical* development of Onsager reciprocal relations for isolated chemical reactors. They convincingly demonstrate that arguments based on *statistical fluctuations, time reversal*, and the principle of *microscopic reversibility* used in all traditional treatments are *nonessential* and, therefore, play no role in the thermodynamic theory of irreversible processes.

3. Teaching the Unified Theory

Obviously, in teaching the unified quantum theory of mechanics and thermodynamics at the graduate level in a single semester course, it is impossible to cover all the various aspects and complexities of this theory as outlined in brief above. Thus, a choice must be made as to which of these and in what detail it makes sense to cover given the limited time available and the background (primarily engineering) of the graduate students taking the course. The choice made by the author was to develop for the students the formalism for the Unified Theory by showing how it allows one to go directly from the elementary problems and solutions of quantum mechanics to the development of the thermodynamic expressions for the thermodynamic properties of gases and to show how this can be done without the use of analogies between statistical and thermodynamic results and without additional hypotheses such as the ergodic hypothesis of statistical mechanics. In doing so, however, the course begins with a brief review of the principal concepts and laws of thermodynamics based on the *non-quantal* exposition given in Gyftopoulos and Beretta (1991, 2005), von Spakovsky and Metghalchi (2006), and von Spakovsky (2005).

3.1 The formalism of thermodynamics

The review given in the first two weeks of my course of the formalism of thermodynamics as a general science applicable to all systems and states begins with very precise definitions of *system*, *property*, and *state*. The first of these is defined 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.

The most general and unambiguous statements of these two laws and their consequences are given in Gyftopoulos and Beretta (1991, 2005), using as primitives space, time, and force or inertial mass. What makes this First Law statement so general and encompassing of all other statements is that it applies to any (separable) system in any (uncorrelated) state undergoing any type of process and only requires as primitives mass (M), the acceleration of gravity (g), and elevation (z)[2]. The implication of this statement of the First Law is the existence of the property called the energy E. Furthermore, from this statement, a number of theorems can be proved such as the fact that E is additive, conserved, and can be formed into balances.

In a similar vein, the Second Law statement given in Gyftopoulos and Beretta (1991, 2005) is completely general[3] and only requires the First Law and precise definitions of system and state which establish $\vec{n}$ and $\vec{\beta}$. No other extensive properties, definitions of cycles and types of interactions, or any other concept are required. 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*. A discussion of these latter properties appears in Gyftopoulos and Beretta (1991, 2005) as well as in the accompanying paper by von Spakovsky and Metghalchi (2006).

Graphically, an illustration of the general science of thermodynamics which emerges from the Unified Theory appears in *Figure 1*. The 3D surface of energy (E), entropy (S), and volume ($\vec{\beta}=\{V\}$) for a simple system of fixed composition ($\vec{n}$) which appears in this figure represents the stable equilibrium states of the system. The *characteristic function* which characterizes this surface is given by

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

or by the *fundamental relation*

$$S = S\left(E,\vec{\beta},\vec{n}\right) \tag{2}$$

From these functions as well as derivative interrelations, all thermodynamic properties can be derived and equations of state developed for any system in a state of stable equilibrium. Examples of interrelations include, of course, the *differential energy relation*, i.e. 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, i.e. the well-known Gibbs relation,

$$dE = TdS + \sum_{i=1}^{r}\mu_i dn_i + \sum_{j=1}^{s} f_j d\beta_j \tag{3}$$

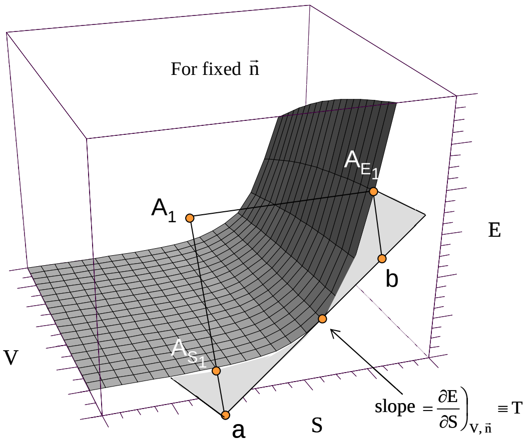

Figure 1. Energy versus entropy versus volume for a simple system of fixed composition.

Equation (3) 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 the case of a simple system for which by definition the fundamental relation (equation (2)) is a homogeneous function of first degree in the variables E, V, and $\vec{n}$ independent of other parameters, one can in addition to equation (3) derive both the Euler and Gibbs-Duhem relations. The latter of these further constrains how changes in the intensive

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[2] For a fully rigorous treatment which includes special relativity, the speed of light c_l in a vacuum also plays a role.

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

properties T, P, and μ_i can be made in moving from one neighboring stable equilibrium state to another along the hyper-surface.

In *Figure 1*, however, it is not just the 3D surface of stable equilibrium states which provides useful information but the vertical axes and the space between the surface and the vertical axes as well which represent all non-equilibrium states and non-stable equilibrium states including those at zero entropy. As a specific illustration, the *generalized adiabatic availability* (Ψ) and *generalized available energy* (Ω) concepts as defined by Gyftopoulos and Beretta (1991, 2005) can be clearly seen in *Figure 1* 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 point "a" on the graph, 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 A_{E_1} of stable equilibrium, the *generalized available energy* Ω_{E_1} (or in this case the *exergy*) is given by the difference in energy between state A_{E_1} and point "b". Clearly, $\Omega_1 > \Omega_{E_1}$, 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*.

The review of the formalism of thermodynamics in this course then concludes with a discussion of the types of interactions a system can undergo (again using 3D surfaces such as in *Figure 1* to illustrate the interactions), global balance equations, equations of state, Legendre transforms, Gibbs' Phase Rule, etc.

3.2 The formalisms and failures of classical physics

In my very brief review of Classical Physics, the formalisms of Newton, Lagrange, and Hamilton are presented as different approaches for achieving the same thing, namely, modeling the time evolution of the states of a purely mechanical system. The Newtonian approach is, of course, a local approach which given an initial state predicts the trajectory of a system (consisting of a single particle or of multiple particles) in time through successive infinitesimal time intervals towards some final state. In contrast, both the Lagrangian and Hamiltonian formalisms are global approaches which calculate the entire trajectory at once. The Lagrangian formalism is then described in some detail as employing a variational principle to arrive at the Euler-Lagrange equations from which the equations of motion for a particular system can be derived. The advantages of this type of global approach over that of the local approach of Newton is that i) it is close to the quantum mechanical (Hamiltonian) approach, ii) from a single scalar (i.e. the Lagrangian) all equations of motion follow, iii) the Euler-Lagrange equations have the same form for any general set of n-independent coordinates, and iv) the conservation laws are more easily obtained in this formalism. Of course, examples are given both for the case of the general potential not being a function of the velocity of the system and for when it is.

The Hamiltonian formalism is then introduced as a Legendre transform of the Lagrangian and as a representation in position and momentum space (as opposed to the Lagrangian's position and velocity space). This is followed by a very brief discussion of the representation of waves via wave functions and a more detailed discussion of the pre-quantum theories of black body radiation with the classical theory prediction resulting in the Rayleigh-Jeans Law for the spectral distribution of radiant energy in a box, which, as can be seen in *Figure 2*, agrees neither with the experimental data nor with Wien's semi-empirical expression. Clearly, something was incomplete with respect to the classical theory.

3.3 The advent of quantum theory

The course, thus, next introduces Max Planck's attempt to correct the classical prediction by speculating that there are only a discrete set of energies

$$\varepsilon_i = ih\nu \quad , \quad i = 0, 1, ..., \qquad (4)$$

that an harmonic oscillator (each wave component in the classical theory is modeled as a single harmonic oscillator) can assume. Although the prediction made by this equation gives the correct result (see *Figure 2*) and matches the experimental data, the form of equation (4) is not correct since $h\nu$ should be multiplied by $(i+1/2)$ and not just i. Nonetheless, the field of quantum mechanics is born and many new and correct results follow, including the conclusions that electromagnetic waves travel in bundles or packets called photons which are particles of zero mass, each photon is described by a wave function but does not behave as classical theory predicts particles to behave, electromagnetic radiation has wave-particle duality, Einstein's quantum mechanical model of the internal energy of monatomic solids is able to closely predict the specific heat data of such solids, matter also has wave-particle duality, the Uncertainty Principle prescribes limits to the spreads or dispersions (not accuracy) of values that can simultaneously be assigned to the characterization of particle position and momentum, etc. The course covers each of these in varying details and then more formally introduces the Hamiltonian formalism of Quantum Mechanics including the concept of operators, observables, expectation values, wave functions, the Schrödinger equation of motion, and the energy eigenvalue problem, i.e. the stationary part of the equation of motion. The latter leads to a presentation in the course of a number of elementary problems in Quantum Mechanics, the solutions to which are then used as the building blocks for the one-particle partition functions, resulting from the Maximum Entropy Principle. It is these building blocks which are briefly discussed next.

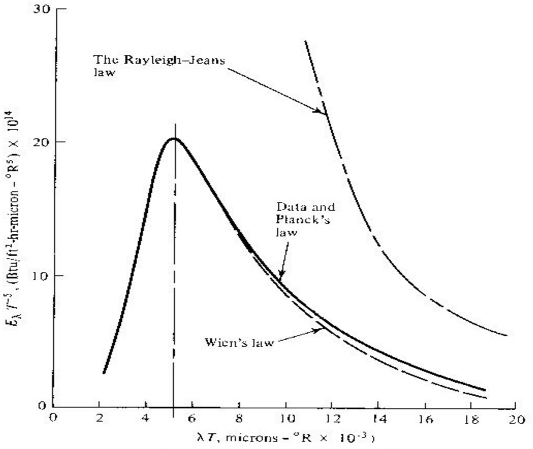


Figure 2. Spectral radiant energy distribution in a box: experimental data, Wien's distribution, the Rayleigh-Jeans prediction, and Planck's initial quantum mechanical prediction (Tien and Lienhard, 1979).

3.4. The unified quantum theory of mechanics and thermodynamics

The Unified Theory is deduced logically from the laws of Quantum Mechanics and Thermodynamics only, allowing one to derive relations between the states or changes of state of a system and its detailed microstructure (Hatsopoulos and Gyftopoulos, 1979). This is done without resort to analogies between statistical and thermodynamic results such as those typically made in statistical thermodynamics between statistical expressions for the entropy and the entropy of classical thermodynamics. This is furthermore done without resort to additional hypotheses such as the ergodic hypothesis of statistical thermodynamics. With this in mind, we proceed to the development which follows.

3.4.1 Elementary problems in quantum physics

The four elementary energy eigenvalue problems presented in detail in the course are i) the free particle in a box, ii) the harmonic oscillator, iii) the rigid rotor, and iv) the hydrogen atom. These are important because they provide the basis for which different modes of energy storage at a particle level are described. The presentation begins with a description of the 1D energy eigenvalue problem for a system of n non-interacting, structureless particles, each of mass m moving along the x-axis, i.e.

$$\sum_{j=1}^{n}\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial {x_j}^2}+V(x_j)\right]u_i = E_i u_i \qquad (5)$$

where the summation and the term in brackets is the Hamiltonian operator, u_i is the i$^{\text{th}}$ energy eigenfunction for the system of particles, and E_i the corresponding energy eigenvalue. The potential energy function V depends on x_j only and noting that $u_i=u(x_1)u(x_2)\ldots u(x_n)$, the *one-particle energy eigenvalue problem* is written as

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial {x_j}^2}+V(x_j)\right]u_j = \varepsilon_j u_j \qquad (6)$$

where

$$E_i = \sum_{j=1}^{n}\varepsilon_j \qquad (7)$$

and ε_j is the *one-particle energy eigenvalue* corresponding to the j$^{\text{th}}$ *one-particle energy eigenfunction* u_j. When V is independent of the position x_j, the equation of motion describes a free particle. It is this free particle in a box or potential well that is the first elementary problem solved in 1D and then generalized to 3D, resulting in an energy eigenvalue expressed by

$$\varepsilon_j = \frac{h^2}{8m}\left(\frac{n_x^2}{l_x^2}+\frac{n_y^2}{l_y^2}+\frac{n_z^2}{l_z^2}\right), n_x, n_y, n_z = 1,2,\ldots \qquad (8)$$

where the n_x, n_y, and n_z are quantum numbers and the l_x, l_y, and l_z the lengths of the sides of the box. Expressions for the energy eigenvalues of the other elementary problems are also determined by first developing appropriate expressions for the potential function and then proceeding to find solutions to equation (6). With these expressions in hand, the next step is to determine the set of eigenvalues x_i^0 of the state matrix that maximizes the entropy of a system in a constrained optimization as a function of their corresponding energy eigenvalues E_i. A given x_i^0 is in fact equal to the probability that a given measurement will yield E_i. It is this application of the *Maximum Entropy Principle* which is discussed next.

3.4.2 Maximization of entropy principle

In the course, the Maximum Entropy Principle is used to establish the *canonical distribution* for the stable equilibrium states of a system with a given expectation value of energy and dispersion-free number of particles and constraints, i.e. an ordinary closed system. This is generalized to systems open to the transfer of rest mass or the creation or annihilation of particles within the system. For such systems called *grand systems* by Gibbs, the number of particles and constraints are not dispersion-free and the resulting probability distribution x_i^0 is called the *grand canonical distribution*. It is this last distribution which is used exclusively in our development of thermodynamic property relations for dilute gases. Thus, x_i^0 is determined by maximizing the entropy of the system in a constrained optimization, i.e.

Maximize
$$S = -k\sum_i y_i \ln y_i \tag{9}$$

subject to
$$E = \sum_i y_i E_i \tag{9a}$$

$$\sum_i y_i = 1 \tag{9b}$$

$$n = \sum_k n_k = \sum_k \sum_i y_i n_{k_i} \tag{9c}$$

where the y_i are the probability distributions for the not stable equilibrium states of the system, S is the system entropy, E the expectation value of the system energy, n_k the expectation value of the number of particles of constituent “k”, n the expectation value of the total number of system particles, and n_{k_i} the number of particles with energy eigenvalue E_i. Using Lagrange’s method of undetermined multipliers, the constrained optimization of equations (9) is transformed into an unconstrained optimization which results in an expression for our *grand canonical distribution*, namely,

$$y_i \to x_i^0 = e^{\left(\sum_k \mu_k n_{k_i} - E_i^0\right)/(kT)} / Q_g \tag{10}$$

where
$$Q_g = \sum_i e^{\left(\sum_k \mu_k n_{k_i} - E_i^0\right)/(kT)} \tag{11}$$

and Q_g is called the *grand canonical partition function* while the energy E and the entropy S of the system are given by

$$E = \left(\sum_i e^{\left(\sum_k \mu_k n_{k_i} - E_i^0\right)/(kT)} E_i^0 \right) / Q_g \tag{12}$$

and
$$S = \frac{E}{T} - \sum_k \frac{\mu_k}{T} n_k + k \ln Q_g \tag{13}$$

3.4.3 Stable equilibrium thermodynamic property relations for dilute gases

In the course, equations (10) and (11) are next utilized to find specific expressions for the thermodynamic stable equilibrium properties of one-component, dilute gases. To do so, the one-particle energy eigenvalue problem defined in equation (6) is used to determine the one-particle energy eigenstates, which can be combined to approximate the energy eigenstates of a dilute gas. This is done by first rewriting equations (10) in terms of the number of particles ν_{ij} with one-particle energy eigenvalue ε_j, i.e.

$$x_i^0 = \frac{e^{\sum_j \nu_{ij}\left(\mu - \varepsilon_j\right)/(kT)}}{Q_g} \tag{14}$$

where
$$Q_g = \sum_i e^{\sum_j \nu_{ij}\left(\mu - \varepsilon_j\right)/(kT)} \tag{15}$$

The expectation value of the number of particles in the one-particle energy eigenstate of energy ε_j is given by

$$\nu_j = \sum_i x_i^0 \nu_{ij} \tag{16}$$

where ν_j is also the one-particle distribution function. The expectation value of the number of particles of the dilute gas is

$$n = \sum_i x_i^0 n_i = \sum_j \nu_j \tag{17}$$

Two types of particles are now considered: *bosons* and *fermions*. One-particle energy eigenstates can be occupied by any number of bosons (e.g., photons) so that $\nu_{ij} = 0,1,2,...$ for all i and j, while only one fermion (e.g., an electron) can occupy such a state at a time. Thus, in this case, $\nu_{ij} = 0,1$ for all i and j. The resulting *grand canonical partition* and *distribution functions* for each of these types of particles are then found to be

$$Q_g = \prod_j \left(1 \pm e^{\left(\mu - \varepsilon_j\right)/(kT)}\right)^{\pm 1} \tag{18}$$

and

$$\nu_j = \left[e^{(\varepsilon_j - \mu)/(kT)} \pm 1 \right]^{-1} \qquad (19)$$

where the plus of ± is for fermions and the minus for bosons. Note that when the dilute gas consists of bosons, the expression for ν_j is called the *Bose-Einstein factor*, while for a dilute gas composed of fermions, ν_j is called the *Fermi-Dirac factor* (Hatsopoulos and Gyftopoulos, 1979). Furthermore, note that in all textbooks based on the statistical paradigm of thermodynamics (e.g., see Tien and Lienhard, 1979), these factors are referred to as Bose-Einstein or Fermi-Dirac statistics since these texts interpret these results in the context of the statistical mechanical approach. However, consistent with the Unified Theory developed by Gyftopoulos and Hatsopoulos and their coworkers, equations (18) and (19) require no such interpretation since the grand canonical distribution on which they are based are the set of eigenvalues x_i^0 of the state matrix that maximizes the entropy of a system. As noted above, a given x_i^0 is in fact equal to the probability that a given measurement will yield the energy eigenvalue E_i. Thus, no statistical interpretation is required here.

3.4.3.1 Perfect, Ideal, and Sommerfeld gases

In the course, three types of gas models are presented: perfect, semi-perfect (or ideal), and Sommerfeld. These models are based on the following set of four approximations: i) the Boltzmann approximation, ii) the constant-potential approximation, iii) the point-particle approximation, and iv) the continuous eigenvalue-spectrum approximation. The perfect gas model requires all four; the semi-perfect gas i), ii) and iv); and the Sommerfeld gas ii), iii), and iv).

The Boltzmann approximation assumes that

$$\frac{\mu - \varepsilon_0}{kT} << 0 \qquad (20)$$

where ε_0 is the ground state energy eigenvalue. This approximation leads to a simplification in expressions for the equation of state and the number of particles n of the dilute gas such that

$$\frac{PV}{kT} \cong e^{\mu/(kT)} q \cong n \qquad (21)$$

where

$$q \equiv \sum_j e^{-\varepsilon_j/(kT)} \qquad (22)$$

and q is defined as the *one-particle partition function*.

The constant-potential approximation assumes that the one-particle energy eigenvalues ε_j can be written as the sum of two parts, i.e. one which is determined as if an externally applied field and long-range forces acting on each particle did not exist and the other which is assumed to be equal to the average potential energy per particle due to an applied field and long-range forces. The first part is further subdivided into the sum of two parts, namely, that due to the translational degrees of freedom, ε_k, and that due to the internal degrees of freedom (e.g., vibration, rotation, etc.), ε_s.

The third approximation, the point-particle approximation, consists of replacing the internal energy spectrum ε_s by a g-fold degenerate average value of $\bar{\varepsilon}_o$ and the summation over the internal degrees of freedom in equation (22) by the degeneracy g. The fourth approximation leads to the replacement of the three summations over the translational degrees of freedom in equation (22) with integrals and requires that to do so the characteristic temperature for translation be much less than one, i.e.

$$\Theta_t \equiv \frac{h^2}{8mkl^2} << 1 \qquad (23)$$

where l represents the different lengths of equation (8).

With these approximations and the previous developments beginning with Section 3.4.1, expressions are found for n and PV/kT for all three types of gases which in turn lead to, for example, the *Sommerfeld equation* for the average energy per electron, $\bar{\varepsilon}$, for a gas of free electrons in a metal, i.e.

$$\bar{\varepsilon} = \frac{3}{5} \Delta\varepsilon^* \left[1 + \frac{5}{12} \left(\frac{\pi kT}{\Delta\varepsilon^*} \right)^2 + \ ... \right] \qquad (24)$$

where $\Delta\varepsilon^*$ is the Fermi level or energy of the gas. With this equation, for example, a linear expression for the contribution of the electron gas to the specific heat of a metal is found as T approaches 0 ^{o}K. It is given by

$$c_{v_{electrons}} = AT = \frac{\pi^2 Rk}{2\Delta\varepsilon^*} T \qquad (25)$$

In this equation, A and $\Delta\varepsilon^*$ are constants specific to a particular material. Equation (25) can be used to modify *Debye's expression* for the specific heat of the metal as T approaches 0 ^{o}K so that the electron gas contribution is taken into account. Thus,

$$c_{v_{metal}} = AT + BT^3 \qquad (26)$$

where B is a constant as well.

In a like manner, the expressions found for n and PV/kT for a semi-perfect gas lead, for example, to the *Sakur-Tetrode equation* for the entropy S of a monatomic gas, namely,

$$S = kn\left\{\ln\left[\frac{kT}{P}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + 5/2\right\} \qquad (27)$$

This last expression is, of course, not appropriate for polyatomic, semi-perfect gases, since it does not include contributions due to the internal degrees of freedom of such gases. Thus, the students are next shown how equation (27) can be modified to account for rotational, vibrational, electronic, and dissociational degrees of freedom. This discussion also includes material on how the elementary energy eigenvalue problems discussed in Section 3.4.1 and used to construct expressions such as equations (24) to (27) must be modified to account for such things as i) the reference energy of the vibrational mode of energy storage, ii) the nuclear spin of nuclei and whether or not the spin is symmetric or anti-symmetric, iii) non-linear harmonics, iv) rotational-vibrational coupling, v) centrifugal stretching, and vi) the 2D or 3D geometry and symmetry of the molecule. This part of the course then concludes with the development of expressions for the chemical potential, entropy, internal energy, and specific heats of a perfect gas.

3.4.3.2 Mixtures of ionized and dissociated perfect and semi-perfect gases

The course next presents multi-component systems, using a binary ionized mixture of perfect gases for purposes of illustration. This is later extended to semi-perfect gas mixtures and to gas mixtures involving dissociation only. Focusing on an ionized mixture of perfect gases which comprises an isolated system in which the following reaction mechanism is active:

$$X \Leftrightarrow X^{+} + e^{-} \qquad (28)$$

it is clear that the presence of ions and electrons in the system results in a non-uniform electric field of potential ψ and, therefore, the system is heterogeneous. However, at high temperatures and low pressures, this system can be divided into independent homogenous parts each of which behaves as a perfect gas, i.e. it behaves as a Gibbs-Dalton mixture.

At stable chemical equilibrium, this mixture must obey the stable equilibrium condition

$$\mu_a - \mu_i - \mu_e = 0 \qquad (29)$$

where the total potential of the atom is equal to its chemical potential and those of the ion and electron are given by

$$\mu_i = q_i\psi + \mu_{c_i} \qquad (30)$$

$$\mu_e = q_e\psi + \mu_{c_e} \qquad (31)$$

Here, the q are the positive and negative charges of the ion and electron. Due to conservation of charge, the total potentials in equation (29) are replaced with the chemical potentials of each species and using the characteristic function for the chemical potential developed earlier in the course for a single constituent perfect gas, the well-known *Saha equation* for a single ionization is derived in terms of the degree of ionization α, i.e.

$$\frac{\alpha^2}{1-\alpha^2} = \frac{2\left(2\pi m_e\right)^{3/2}}{h^3}\frac{\left(kT\right)^{5/2}}{P}\exp\left(\frac{-\Theta_I}{T}\right) \qquad (32)$$

where Θ_I is the characteristic temperature of ionization. A plot of the variation of α with T and P for monatomic oxygen appears in *Figure 3*. This is typical of the types of plots that the students are asked to generate once they have derived similar expressions for the degree of ionization of a mixture of semi-perfect gases or the degree of dissociation of a mixture of semi-perfect or perfect gases. This part of the course then ends with a discussion of the partial pressures of the constituents of the ionized mixture, i.e. that for the atom being uniform throughout the mixture and those for the ion and electron varying exponentially with ψ. This in turn leads to a development of the electro-static potential distribution in the gas due to a source density, which is governed by Poisson's equation for ψ.

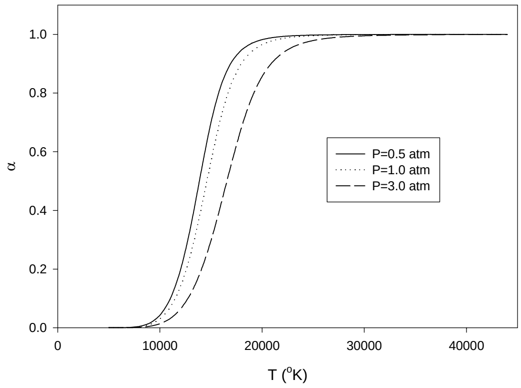


Figure 3. Degree of ionization versus temperature at three different pressures for monatomic oxygen as a perfect gas.

3.4.4 Stable equilibrium thermodynamic property relations for dense gases

In the final part of the course, the students are shown how the thermodynamic properties for dense gases are developed. For such gases, the constant-potential approximation used in the development of our expressions for dilute gases is no longer applicable and the particles no longer behave independently. It is, thus, necessary to introduce an intermolecular potential function to the earlier developments, a function which must be increasingly accurate the denser the gas becomes. The one-particle partition function, equation (22), now becomes a *multi-particle partition function* by defining the energy eigenvalue ε_j as

$$\varepsilon_j = \sum_{i=1}^{n_p}\varepsilon_{i_s} + \sum_{i=1}^{n_p}\left(\frac{|\vec{p}_i|^2}{2m}\right)_j + \phi_j\left(r_1,\ldots,r_{n_p}\right) \qquad (33)$$

where n_p equals one if only two-body interactions are considered, two for three-body interactions, etc. The first term to the right of the equals accounts for the energies associated with the internal degrees of freedom of the n_p +1 particles, while the second term accounts for those associated with the translation degrees of freedom of these particles. The last term accounts for the inter-particle interactions. Substitution of equation (33) into (22) results in the *multi-particle partition function*, q, which can be shown for the case of n_p =1 to be the product of that due to internal degrees of freedom, q_s, translational degrees of freedom, q_t, and inter-particle interactions, q_ϕ, i.e.

$$q = q_s q_t q_\phi \qquad (32)$$

The functional forms taken by q_s and q_t are those developed earlier for the one-particle partition functions while q_ϕ can be shown to be given by

$$q_\phi = \left[1 - \frac{nb(T)}{V}\right] \qquad (33)$$

where V is the volume of the system and $b(T)$ is the second virial coefficient defined by

$$b(T) = 2\pi\int_0^\infty \left(1 - e^{-\phi/(kT)}\right) r^2 dr \qquad (34)$$

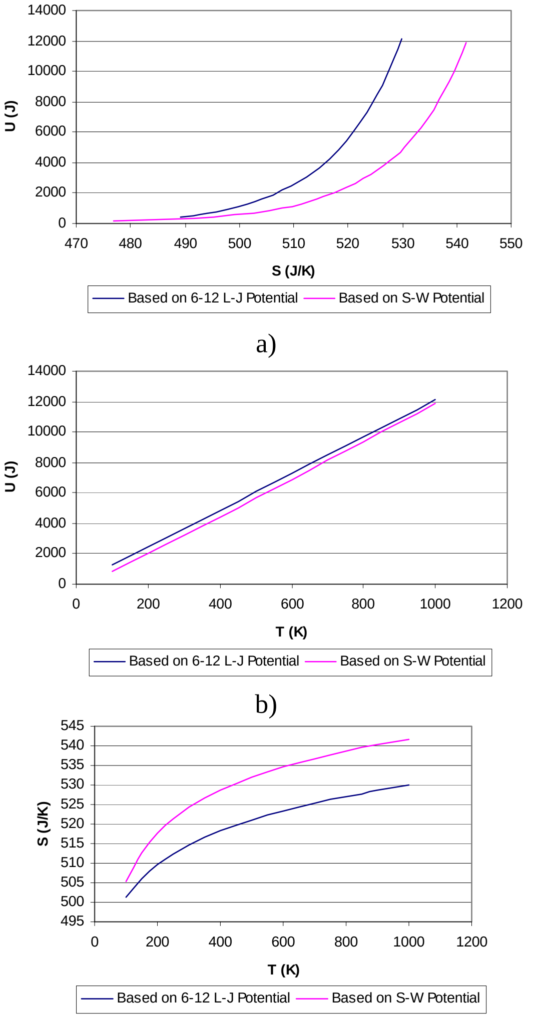
Based on earlier developments in the course, these last equations can be used then to derive an expression for the fundamental relation of the dense gas from which in turn one can derive the virial equation of state given by

$$P = \frac{nkT}{V}\left[1 + \frac{nb(T)}{V} + \frac{n^2 b^2(T)}{V^2} + \ldots\right] \qquad (35)$$

Of course, to finalize these expressions, some model must be chosen for the inter-particle potential, and, thus, the students are introduced to a variety of angle-independent (symmetrical) and angle-dependent (asymmetrical) semi-empirical functions such as the hard sphere, Sutherland, point-center-of-repulsion, square well, Lennard-Jones, Buckingham, Keeson, and Stockmayer potentials. The students then use these in order, for example, to generate two-dimensional slices (e.g., see *Figure 4*) in the energy-entropy plane of the E-S-$\vec{\beta}$-$\vec{n}$ hyper-surface of stable equilibrium states of the system.

4. Conclusions

It has often been said that *thermodynamics* is a particularly difficult science to learn but more importantly to understand. It was in trying to address this latter point that I became intrigued by the Unified Theory, a theory that presents thermodynamics as a broad and general science not limited to certain types of systems (large) nor to certain types of states (stable equilibrium).



a)

b)

c)

Figure 4. Comparison of the results obtained for 1 mole of He contained in a 3 cm^3 tank using a dense gas model based on the Lennard-Jones potential and the square-well potential, respectively: a) 2D slice in the energy-entropy plane of the hyper-surface of all possible stable equilibrium states of the system; b) internal energy versus temperature; and c) entropy versus temperature.

As should be evident from the presentation given above, the Unified Theory allows one to arrive at the same thermodynamic property relationships as are typically found with the statistical based paradigm but without the encumbrance of this additional discipline, i.e. that of statistical mechanics. It simply is not needed and in fact its inclusion results, as outlined above and in the literature cited, in a number of paradoxes and inconsistencies which the Unified Theory does not have. With the latter, in fact, thermodynamics can be taught as a science which applies to any system large or small and to any state, demolishing the boundary (using the terminology of statistical mechanics) between the microscopic and the macroscopic. It is a science in which entropy is a fundamental property of matter, stable equilibrium is a state of perfect order not disorder, and irreversibilities are not a “macroscopic invention” but instead occur at the microscopic level. It is this broader science of thermodynamics, which I have taught to my graduate students over the last several years both in its non-quantal and quantal versions and which I believe has provided them with a much clearer and broader understanding of this science. As a next step in this process, I am developing a third graduate level course which specifically addresses the Beretta equation, its experimental verification, and the general mathematical framework of the Unified Theory.

Nomenclature

b	second virial coefficient
c_v	specific heat at constant volume
E	energy
E_i	energy eigenvalue
f	generalized force
g	acceleration of gravity or degeneracy
h	Planck’s constant
$\hbar$	modified Planck’s constant
k	Boltzmann’s constant
l	length
M	inertial mass of a weight
m	mass
$\vec{n}$	set of amounts of constituents
n	expectation value of the number of particles
n_k	expectation value of the number of particles
n_{ki}	the number of particles
$n_{x,y,z}$	quantum numbers
P	pressure
p	momentum
Q_g	grand canonical partition function
q	multi- or one-particle partition function
R	universal gas constant
r	distance
S	entropy
T	temperature
t	time
u_i	energy eigenfunction
V	volume or potential
x_i^0	probability distribution for stable equilibrium states; eigenvalue of the state matrix
y_i	probability distribution for not stable equilibrium states
z	elevation in a gravity field

Greek Letters

α	degree of ionization
$\vec{\beta}$	set of parameters
ε	energy eigenvalue or quantum of energy
ε_k	translational energy eigenvalue
$\bar{\varepsilon}$	average energy per electron
$\bar{\varepsilon}_o$	average energy eigenvalue
ε_s	internal energy eigenvalue spectrum
ϕ	interparticle potential
μ	total or chemical potential
ν	frequency
ν_j	one-particle distribution function
ν_{ij}	number of particles with one-particle energy eigenvalue ε_j
Ω	generalized available energy
Ψ	generalized adiabatic availability
ψ	electrostatic field potential
Θ	characteristic temperature

Subscripts

a	atom
e	electron
ϕ	interparticle potential
I	ionization
i	ion
s	internal degrees of freedom
t	translation degrees of freedom

Superscripts

0	stable equilibrium

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