THERMODYNAMICS AS A NON-STATISTICAL THEORY

by

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Abstract

An investigation of the recently proposed theory of quantum thermodynamics which encompasses both mechanics and thermodynamics within a single mathematical structure is presented.

The first part of the investigation is devoted to establishing the mathematical expression for entropy. Upon determining the conditions that must be satisfied by entropy, we find that the only expression suitable for the purposes of quantum thermodynamics is the one proposed by von Neumann.

In the second part of this dissertation, we investigate the dynamical law of quantum thermodynamics. Several conditions that must be satisfied by the equation of motion are determined, and equations proposed in the literature are investigated in the light of these conditions. We conclude that only an equation proposed by Beretta satisfies all the requirements.

The third part of our investigation involves a comparison of experimental results on relaxation phenomena with the predictions of the Beretta equation. We show that the predictions are consistent with experiments performed on dilute systems, and suggest additional specific experiments for more definitive validation of quantum thermodynamics.

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Chapter 1

1. Introduction

Recently a new theory that encompasses within a single mathematical structure both mechanics and thermodynamics has been proposed [Hatsopoulos, Gyftopoulos, 1976; Beretta, 1982]. It is called quantum thermodynamics and is a non-statistical interpretation of thermodynamics. It describes both reversible and irreversible phenomena.

The first objective of this dissertation is to establish the mathematical expression for entropy in quantum thermodynamics. It is shown that the expression suggested by Hatsopoulos and Gyftopoulos [1976] is the only acceptable one among the candidate expressions found in the literature.

The second objective is to establish a set of necessary conditions that need to be satisfied by the equation of motion of quantum thermodynamics. These conditions can be used in judging whether a proposed equation of motion is acceptable. Several equations of motion have been proposed in the literature but only the Beretta equation [Beretta *et al* 1984, 1985] satisfies all the known necessary conditions to date. A special class of solutions of the Beretta equation is described and studied.

The third objective is to provide experimental evidence of the validity of quantum thermodynamics. Because quantum thermodynamics admits quantum mechanics as a special case, every experiment that can be explained by quantum mechanics is also explained by quantum thermodynamics. But the converse is not true. Hence a set of experiments in which the predictions of quantum thermodynamics differ substantially from the predictions of quantum mechanics is included. In addition, we discuss the inadequacy of statistical quantum mechanics in explaining these experiments.

Moreover, we investigate some implications of quantum thermodynamics regarding the smallest value of entropy admitted by the stable equilibrium states of a grand system. Finally, we present an unresolved problem related to the triple-point of a pure substance.

The dissertation is structured as follows:

Chapter 2 is devoted to background considerations. In Section 2.1 we present the definition of thermodynamics adopted in this dissertation. In Section 2.2, we review the notions of system, property, state, preparation, ensemble, and measurement. They are essential in formulating any physical theory.

Throughout this dissertation, we use ideas of quantum physics rather than classical physics. The reasons for this choice are presented in Section 2.3, the postulates of quantum mechanics and statistical quantum mechanics in Section 2.4, the currently prevailing statistical understanding of thermodynamics in Section 2.5. It is shown that the current statistical understanding of thermodynamics leads to inconsistencies. Various remedies suggested in the literature are studied and shown to be unsatisfactory.

In Chapter 3 we present a non-statistical approach to thermodynamics which is done in two steps: in Section 3.1, we give the implications of this new understanding of thermodynamics and in Section 3.2, the postulates of a new theory, called quantum thermodynamics, which provides us the mathematical framework to express our ideas.

In Chapter 4 we establish the mathematical expression for entropy in quantum thermodynamics. To achieve this goal, in Section 4.1 we determine a set of conditions that need to be satisfied by the expression for entropy in quantum thermodynamics. In Section 4.2, we review many of the candidates proposed in the literature, and in Section 4.3 we use the criteria to decide which expression is valid. It turns out that only the von Neumann entropy passes this test and, therefore we conclude that it is the desired expression. Upon determining the expression for entropy, we end this chapter by

presenting, in Section 4.4, certain mathematical conditions imposed on the Hamiltonian operator of a system by the expression for entropy.

In Chapter 5 we investigate the dynamical law of quantum thermodynamics. We present a set of conditions that need to be satisfied by the equation of motion in Section 5.1, and proposed equations of motion in Section 5.2. Upon investigating the proposed equations in Section 5.3, we conclude that only one suggested by Beretta satisfies all the stated conditions. In Section 5.4 we present, for the first, a special class of solutions of the Beretta equation.

In Chapter 6 we provide experimental evidence of the validity of quantum thermodynamics. In Section 6.1 we present two spin-relaxation experiments reported in the literature. We show that the results of these two experiments are consistent with the dynamical law of quantum thermodynamics. In Section 6.1.4 we suggest a variation of these two experiments which, we believe, can give an excellent quantitative verification of quantum thermodynamics. In Section 6.2 we show that under suitable conditions the Beretta equation reduces to phenomenological equations of irreversible thermodynamics whose validity is shown in innumerable experiments.

Chapter 7 contains our reflections on two unresolved problems. In Section 7.1, we address a problem related to the value of entropy assigned to stable equilibrium states with zero temperature. In Section 7.2, we investigate an intriguing problem related to triple points of pure substances.

Chapter 8 contains a summary and recommendations for future work.

Chapter 2

2. Background

This chapter contains background considerations that are used frequently in the remaining portions of this dissertation. In Section 2.1, the definition of thermodynamics adopted in this dissertation is presented. Section 2.2 is devoted to a review of the notions of system, property, state, preparation, ensemble, and measurement. These notions are essential in formulating any physical theory.

Throughout this dissertation, we use ideas of quantum physics rather than classical physics. The reasons for this choice are presented in Section 2.3, the postulates of quantum mechanics and statistical quantum mechanics in Section 2.4, the currently prevailing statistical understanding of thermodynamics in Section 2.5. It is shown that the current statistical understanding of thermodynamics leads to inconsistencies. Various remedies suggested in the literature are studied and shown to be unsatisfactory.

2.1 Thermodynamics

In this thesis, we adopt the definition of thermodynamics given by Gyftopoulos and Beretta [1993]: "the study of motions of physical constituents (particles and radiations) resulting from externally applied forces, and from internal forces (the actions and reactions between constituents)." This is identical to the definition of mechanical dynamics [Timoshenko and Young, 1948], and implies that thermodynamics deals with the time evolution of a system in addition to considering the values of the properties of the system at a given instant of time. By virtue of the second law of thermodynamics, the definition encompasses a much broader spectrum of phenomena than mechanical

dynamics. In other words, thermodynamics accounts for phenomena with zero and positive values of entropy, whereas mechanical dynamics accounts only for phenomena with zero values of entropy [Gyftopoulos and Beretta, 1993].

According to this definition, thermodynamics applies to equilibrium as well as non-equilibrium situations. However, the current definition of thermodynamics found in the literature is more restrictive. For example, Guggenheim [1967] defines it as "that part of physics concerned with the dependence on temperature of any equilibrium property." In this dissertation, the branch of thermodynamics restricted to equilibrium situations is called "thermostatics".

Like any physical theory thermodynamics has two parts. The first part is called kinematics, and determines the conditions of a system at a given instant of time. The second part is called dynamics, and establishes relations between the conditions of the physical system at different instants of time. Furthermore, the validity of thermodynamics (as well as any other physical theory) relies on the reproducibility of its results.

Among the phenomena that we would like to describe using thermodynamics are: acceleration of a solid ball in a gravitational field; motion of an electron in the vicinity of a proton; internal discharge of a well-insulated battery; a bunch of gas molecules filling a container of fixed volume; mixing of hot and cold water resulting in luke-warm water.

2.2 Definitions

In this section we give definitions of several concepts - physical constructs - which play a major role in formulating the postulates of the physical theories presented in this dissertation.

2.2.1 System

In any physical study we always focus attention on a collection of constituents that are subject to a nest of forces. When the constituents and the nest of forces are well defined, we call such a collection a <u>system</u>. Everything that is not included in the system we call the <u>environment</u> of the system.

A *system* is defined [Gyftopoulos and Beretta, 1991a] as a collection of constituents, provided it can be determined by the following specifications.

1. The type of each constituent and the range of values of the corresponding amount.

2. The type and the range of values of the parameters that fully characterize the external forces exerted on the constituents by bodies other than the constituents, such as the parameters that describe an airtight container. The external forces do not depend on coordinates of bodies other than those of the constituents of the system.

3. The internal forces between constituents, such as intermolecular forces, and forces that account for chemical and/or nuclear reactions.

For example, a system can be a hydrogen atom in an airtight container of specified dimensions, subject to an external force (e.g., an external magnetic field of known strength), or a ball made out of lead of mass 1 kg, in a gravitational field of specified strength.

2.2.2 Properties

A property is defined as [Gyftopoulos and Beretta, 1991b]: <u>Property</u> is a (system) attribute that can be evaluated at any given instant of time by means of a set of measurements and operations performed on the system which result in a numerical value

- the *value of the property*. This value is independent of the measuring devices, other systems in the environment, and other instants of time.

Two properties are *independent* if the value of one can be varied without affecting the value of the other.

2.2.3 States and Types of States

A novel definition of the concept of state is given by Gyftopoulos and Beretta [1991c]: For a given system, the types and the values of the amounts of all the constituents, the values of the parameters, and the values of a complete set of independent properties encompass all that can be said about the system at an instant of time and about the results of any measurements that may be performed on the system at that instant of time. We call this complete characterization of the system at an instant of time the <u>state</u> of the system.

States can be classified in different categories. One is in terms of their evolution as a function of time [Gyftopoulos and Beretta, 1991d]. An <u>unsteady state</u> is one that changes as a function of time because of interactions of the system with other systems. A <u>steady state</u> is one that does not change as a function of time despite interactions of the system with other systems in the environment. A <u>nonequilibrium state</u> is one that changes spontaneously as a function of time, that is, a state that evolves as time goes on without any effects on or interactions with any other systems. An <u>equilibrium state</u> is one that does not change as a function of time while the system is isolated - a state that does not change spontaneously. An <u>unstable equilibrium state</u> is an equilibrium state that may be caused by to proceed spontaneously to a sequence of entirely different states by means of a minute and short lived interaction that has only an infinitesimal temporary effect on the state of the environment. A <u>stable equilibrium state</u> is an equilibrium state that can be altered to a different state only by interactions that leave net effects in the environment of

the system. If a system is in a stable equilibrium state and is a composite of two or more subsystems, the subsystems are said to be in <u>mutual stable equilibrium</u>. These definitions are identical to the corresponding definitions in mechanics but include a much broader spectrum of states than those encountered in mechanics.

2.2.4 Preparation

To prepare a physical system for study we use, in general, a series of operations. For example, we separate the system from its surrounding by washing the impurities away, we put the system in an oven at a specified temperature, and keep it there for some specified length of time. A set of such operations is called a <u>preparation</u> scheme Π. A preparation scheme is physically acceptable if it is reproducible, since reproducibility is an essential feature of physics. Our aim in repeating the same preparation scheme Π is to achieve the same state. However, the preparation may be such as not to yield the same state.

2.2.5 Ensemble

The validity of any physical theory relies on the reproducibility of its results. This necessitates the study of a set of replicas of a physical system rather than an individual system. Furthermore, the probabilities inherent to the nature of a system can only be investigated using a statistical analysis involving a large number of replicas. Therefore, a set of identically prepared replicas of a physical system plays an essential role in physics, and is called an <u>ensemble</u> E.

In generating the ensemble E, we repeat the same preparation scheme Π aiming at having the same state. If we are successful, then every member of the ensemble E is in the same state, and the ensemble is called a <u>homogeneous ensemble</u>. However, if we fail

to achieve the same state, different members of the ensemble E are in different states than the rest of the members. Such an ensemble is called a <u>heterogeneous ensemble</u>.

2.2.6 Measurement

<u>Measurement</u> is a reproducible ordered set of operations performed on a system at a given instant of time, in order to gain information about a definite property of the system at that instant of time. In this dissertation, a <u>measurement result</u> is a precise numerical value.

Measurements are the essential tools in determining the state of a system. Hence they are indispensable to establish whether an ensemble E generated by repeating the same preparation scheme Π is homogeneous or heterogeneous. This point has been especially emphasized by von Neumann [1955]. We can always conceive of many subdivisions of the ensemble E into subensembles; each subensemble must contain an 'effectively infinite' number of systems so that we can get an accurate statistical description of the measurement results obtained from each of the subensemble. The ensemble E is <u>homogeneous</u> if the probabilistic description of all measurement results obtained from each of its subensemble is identical to the probabilistic description of measurement results obtained from the ensemble E itself. Otherwise, the ensemble E is <u>heterogeneous</u>.

2.3 Quantum Physics versus Classical Physics

In this dissertation, we base our discussions on quantum physics rather than classical physics. There are several reasons for this choice. The first is the success of statistical quantum mechanics in describing properties of thermodynamic equilibrium states [Gyftopoulos and Beretta, 1993]. Statistical classical mechanics was not as successful as statistical quantum mechanics. For example, Gibbs' paradox can only be

resolved if quantum effects are taken into account. There are other examples where the predictions of statistical quantum mechanics and statistical classical mechanics are extremely different and even contradictory. To show that, consider a bunch of gas molecules in an airtight container. If the system is in thermodynamic equilibrium, i.e., the gas is at some temperature T and pressure P, according to the classical kinetic theory of gases the molecules move continuously. However, statistical quantum mechanics predict that the value of linear momentum associated with every molecule is zero, hence not even a single gas molecule moves. Clearly, only one of these two pictures can be correct, and it is the latter one that is consistent with the definition of equilibrium given in Section 2.2.3.

The second reason is that serious difficulties are encountered with the statistical classical mechanical expression for entropy. Here, we mention briefly these difficulties without presenting any details. A more complete discussion can be found in the "General Properties of Entropy" by A. Wehrl [1978]. The so-called classical continuous expression for entropy can take negative values in contrast to the thermodynamic entropy which is always non-negative. This difficulty leads Wehrl to conclude that " not every classical probability distribution can be observed in nature." Among the probability distributions that cannot be observed in nature are the pure states of classical mechanics (delta functions in the phase space). However, this implies that classical mechanics cannot be used in describing natural phenomena, and yet we know that classical mechanics has been a very successful theory. Another difficulty with the classical continuous expression for entropy is its lack of 'monotinicity'.

These difficulties can be overcome by using the classical discrete entropy, but then an approximation is introduced and the value of entropy depends on both the probability distribution and the discretization scheme.

The third reason for working within the framework of quantum physics is its broader application range compared to classical physics. For example, the results of

classical mechanics can also be described by quantum mechanics. However, there are phenomena that can be described by quantum mechanics but not by classical mechanics, such as the two-slit experiment. Therefore, if the motions of physical constituents resulting from externally applied and internal forces can be described within the framework of quantum physics, there is no need to study these motions in classical physics.

2.4 Postulates of Quantum Mechanics and Statistical Quantum Mechanics

In this section we present the postulates of conventional quantum mechanics and statistical quantum mechanics. Time evolution of a system whose initial state is known with certainty is studied within the framework of quantum mechanics. However, if some uncertainty is involved about the initial state, we use the laws of statistical quantum mechanics to describe the behavior of the system.

2.4.1 Postulates of Quantum Mechanics

Postulate 1.   *Systems*

With every system there is associated a complex, separable Hilbert space H. denoting the countable infinity by $\aleph_0$, either dim(H)= $\aleph_0$, or dim(H)=n in which case H is equivalent to an n-dimensional complex Euclidean space C^n [Conway, 1985].

The Hilbert space associated with a composite system of two independent subsystems A and B which are associated with Hilbert spaces H_A, H_B, respectively, is the direct product $H_A \otimes H_B$.

Postulate 2.   *Properties and Observables*

Among the properties associated with a system, there is a special class of them called the <u>observables</u>. They are associated with linear, self-adjoint, closed operators

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{H,I,J,...} on the Hilbert space H. Using spectral theory, we can express each of these operators in the following form:

$$J = \int \lambda \, dE(\lambda),$$
(2.1)

where the set $\{\lambda\}$ is the spectrum of J, and $dE(\lambda)$ is a projection-valued measure.

The spectrum of each such operator is non-empty and real. If dim(H)=n, the spectrum of any operator J correponding to an observable is purely point spectrum, and the elements of the spectrum $\{\lambda\}$ are called the eigenvalues of J. If dim(H)=$\aleph_0$, because the residual spectrum of a self-adjoint operator is empty [Rudin, 1973], the spectrum of J can be decomposed into two parts: the point spectrum and the continuous spectrum. It can so happen that either of these two sets is empty, in which case we say that J has purely continuous (or, point) spectrum, respectively. Again, the elements of the point spectrum are called the eigenvalues of J [Conway, 1985].

As explained in Section 2.2.6, upon measurement of a property performed on a system we always get a precise number. If this property is an observable, the measurement result is necessarily in the spectrum of the operator which is associated with that observable. For example, if the operator associated with the observable is J (Equation (2.1)), then the measurement result is in the set $\{\lambda\}$.

An important implication of the superselection rules [Wick *et al*., 1952] is the existence of linear, self-adjoint, closed operators that do not correspond to physical observables. Furthermore, if the dimension of the Hilbert space is $\aleph_0$, some operators that correspond to observables are unbounded, hence they are not continuous. Examples of such operators are the Hamiltonian, the position and the linear momentum operators. All the linear operators on a finite-dimensional Hilbert space are bounded, hence continuous [Conway, 1985; Rudin, 1973].

Postulate 3.   *State*

We have shown in Section 2.2 that to every system, prepared according to a preparation scheme Π that generates a homogeneous ensemble E, there corresponds a state. State in quantum mechanics is the set ε of instantaneous operators that correspond to observables and an element ψ of the Hilbert space H with unit-norm (i.e., $\|\psi\| = 1$). To every unit vector ψ of H, there corresponds a unique operator P_ψ, which is an orthogonal projection onto the one-dimensional subspace of the Hilbert space H, spanned by the vector ψ. In Dirac notation

$$P_\psi = |\psi\rangle\langle\psi|. \tag{2.2}$$

Therefore, in representing the state, we can use the projection operator P_ψ instead of the vector ψ. By definition, a projection operator on a Hilbert space is bounded, self-adjoint, and idempotent [Conway, 1985], and is called a <u>pure state</u>.

If a measurement of an observable is performed on a system in state $\{\varepsilon,\psi\}$, and the operator associated with the observable is J (Equation (2.1)), the probability of getting a measurement result between j and j+dj is

$$\int_j^{j+dj} \lambda\langle\psi, dE(\lambda)\psi\rangle = \int_j^{j+dj} \lambda\, dE_\psi(\lambda) \tag{2.3}$$

where $< , >$ denotes the inner product in the Hilbert space H. An immediate conclusion is that the arithmetic mean value <J> of the data yielded by measurements of the observable on the ensemble E is given by the inner product (or alternatively by the trace operation)

$$\langle J\rangle = \langle\psi, J\psi\rangle = \text{Tr}\big(JP_\psi\big). \tag{2.4}$$

Postulate 4.   *Time Evolution*

For every system there exists a linear, self-adjoint, closed operator H on the Hilbert space H, called the Hamiltonian operator, that is the generator of motion. The time evolution of the system is unitary and is governed by the Schrödinger equation:

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \tag{2.5}$$

or, equivalently,

$$i\hbar\frac{\partial P_\psi}{\partial t} = \left[H, P_\psi\right]. \tag{2.6}$$

2.4.2 Postulates of Statistical Quantum Mechanics

There are situations in which some uncertainty is involved about the state of a system. For example, the state of a system prepared according to a scheme Π which generates a heterogeneous ensemble is ambiguous. The typical situation encountered in statistical quantum mechanics is the following: Initially, the system is in state-1 with probability p_1, in state-2 with probability p_2, etc... This information allows us to perform a statistical study of the behavior of the system using quantum mechanics and statististics.

A helpful way of visualizing the study of a system whose initial state is ambiguous involves ensembles. We consider a heterogeneous ensemble E in which fraction p_1 of the members are in state-1, fraction p_2 of the members are in the state-2, etc... We can then study the behavior of each member of the ensemble E using quantum mechanics.

Postulate 1.   *Systems*

This postulate is identical to the first postulate of quantum mechanics. Thinking in terms of ensembles, members of the heterogeneous ensemble E are identical systems, hence the same Hilbert space H is associated with every one of them.

Postulate 2.   *Properties and Observables*

This postulate is identical to the second postulate of quantum mechanics.

Postulate 3.   *Statistical State*

For simplicity, we assume that the instantaneous operators that correspond to observables are identical in every member of the ensemble E (this is customary in the literature). Then, in addition to the set ε of operators (common to all members of the ensemble E) associated with observables, the statistical state is represented by a linear, self-adjoint, non-negative definite, unit-trace operator on the Hilbert space H which is denoted by ρ and is a linear superposition of projection operators:

$$\rho = \sum_i p_i P_{\psi_i} . \tag{2.7}$$

where $P_{\psi_i} = |\psi_i\rangle\langle\psi_i|$.

If a measurement of an observable is performed on the system described by the statistical state $\{\varepsilon,\rho\}$, and the operator associated with the observable is J (Equation (2.1)), the probability of getting a measurement result between j and j+dj is

$$\sum_i p_i \int_j^{j+dj} \lambda \langle \psi_i, dE(\lambda)\psi_i \rangle = \sum_i p_i \int_j^{j+dj} \lambda dE_{\psi_i}(\lambda) . \tag{2.8}$$

This implies that the arithmetic mean value <J> of the data yielded by measurements of the observable on the ensemble E is given by the inner product (or alternatively by the trace operation)

$$\langle J \rangle = \sum_i p_i \langle \psi_i, J\psi_i \rangle = \sum_i p_i Tr(P_{\psi_i}) = Tr\left(J \sum_i p_i P_{\psi_i}\right) = Tr(J\rho). \qquad (2.9)$$

Postulate 4. *Time Evolution*

The time evolution in a statistical theory is uniquely determined by the time evolution postulated in the physical theory (quantum mechanics), since every homogeneous subensemble obeys that evolution. Therefore, the equation of motion in statistical mechanics, called the von Neumann equation, is derived from the Schrödinger equation [von Neumann, 1955] and is:

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho]. \qquad (2.10)$$

2.5 Thermodynamics as a Statistical Theory

In this section, we review the prevailing statistical interpretation of thermodynamics. Moreover, we examine the difficulties encountered with this interpretation and review the remedies suggested in the literature.

The prevailing understanding of thermodynamics is that it is a statistical theory of mechanics that applies only to macroscopic systems in equilibrium. Said differently, it is a 'simplified language' that provides us with a 'reduced description' of macroscopic systems. It is a practical alternative to the complicated and time consuming approach of studying the behavior of complex systems mechanically. Furthermore, the initial

conditions of a complex macroscopic system are hard to reproduce and, therefore, it is not interesting to study the behavior of such systems in detail using the laws of mechanics.

An implication of a statistical treatment of thermodynamics has been paraphrased by Gyftopoulos and Hatsopoulos [1980] as follows: "In reality, matter does not have entropy as a property as it has, for instance, energy and momentum as properties. Entropy is an engineering, nonphysical concept applicable to very large systems only. For such systems, scientists and engineers have neither the tools nor the time to analyze the systems in detail. For this reason, they resort to statistical estimates - introduce subjective probabilities which reflect the ignorance of the professionals - and a measure of the degree of ignorance in each case is entropy."

In statistical quantum mechanics entropy is defined by

$$I_v = -k \ Tr\big(\rho \ Log(\rho)\big). \tag{2.11}$$

This formula is due by von Neumann [1927]. The meaning assigned to this expression is "a measure of the amount of chaos within a quantum-mechanical state" [Wehrl, 1978]. The heterogeneous ensemble E is conceived of as a statistical mixture of homogeneous subensembles . Members of a subensemble are in an eigenstate $\{\varepsilon,\psi_i\}$ of the statistical state operator, and the fraction of the members of the subensemble E_i among the members of the ensemble E is the eigenvalue p_i of the state operator that corresponds to the eigenstate $\{\varepsilon,\psi_i\}$.

As mentioned earlier, statistical quantum mechanics had great success in describing the properties of thermodynamic equilibrium states (in this dissertation referred as stable equilibrium states), i.e., it is a good description of thermostatics. However, the dynamical part of the theory is not as successful as its kinematics. This point is explained by Wehrl [1978] as "A very common formulation of the second law of thermodynamics reads as follows: the entropy of a closed system never decreases; it can

only remain constant or increase... (this statement is), however, in striking contradiction to the fact that the entropy of a system obeying the Schrödinger equation *always remains constant*... This result seems to be absurd since one knows by experimental experience that the second law is something very sensible and very useful. There is one way out of this dilemma; that is, that the time evolution of a system is not described by the Schrödinger equation but by some other equation. In fact, in statistical mechanics one uses, with great success, equations like the Boltzmann equation, the master equation, and other equations."

In the remaining part of this section, we present different remedies (or approaches) to resolve the problem just cited that have appeared in the literature within the framework of statistical quantum mechanics. An excellent review of these different approaches has been given by Park and Simmons [1981]. We show that none of the remedies is a satisfactory explanation of the discrepancy pointed out by Wehrl.

2.5.1 Information Theoretic Approach

Jaynes [1957a, b] is the chief advocate of the information theoretic approach to thermodynamics. According to this school of thought, entropy is a measure of the amount of information that an observer has about the actual state of the system, and the entropy increase in a closed system represents essentially the growing obsolescence of past knowledge rather than an objective dynamical process.

According to the information-theoretic approach, the 'thermodynamic state' is conceived of as the best description of the state of knowledge of an observer possessing only partial information about the 'actual state' in which the system is. To every 'actual state' $\{\varepsilon, \psi_i\}$ of the system which is consistent with the partial information that the observer has, a probability p_i is assigned. A measure has been defined for the amount of

information that an observer has about the actual state of the system. This measure is called 'entropy', denoted by I_S, and given by the expression [Shannon, 1948]:

$$I_S = -k \sum_i p_i \text{Log}(p_i).$$ (2.12)

It is postulated that the measure of information represents the thermodynamic 'entropy'. This expression is equivalent to I_V given by Equation (2.11), if the only actual states that are present in the heterogeneous ensemble are the eigenstates of the statistical state operator (and the mixing coefficients are the respective eigenvalues). However, this is not necessarily the case in statistical quantum mechanics (due to non-unique decomposition of a statistical state into pure states, as explained in Appendix A). To avoid this difficulty, in the information-theoretic approach of Jaynes, states other than the eigenstates are excluded from the study based on the belief that they do not represent 'mutually exclusive events' [Jaynes, 1957b].

In Jaynes' approach to thermodynamics, a set of probabilities is assigned to 'actual states' of the system according to the partial information that the observer has. The type of information is restricted to the values of certain properties (especially energy). For example, if the observer knows the value of the energy of the system, only the 'mutually exclusive events' represented by the eigenfunctions of the Hamiltonian are associated with non-zero probabilities. However, the system can very well be in a state with the specified value of energy and yet not an energy eigenstate. This possibility is excluded in Jaynes' approach where 'the best, unbiased description of the system' is considered.

Furthermore, according to Jaynes, among the means an observer uses to get a partial information about the 'actual states' of the system is to perform a macroscopic measurement such as a temperature measurement. Being able to find the value of energy upon performing a single measurement is rather contradictory within the framework of

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quantum mechanics in which measurement results are described probabilistically (Section 2.3.1).

The understanding of thermodynamics presented in this dissertation is incompatible with this approach. Throughout this thesis, entropy is treated as a property of the system. Therefore, we would like to emphasize the conceptual difference between Jaynes' and our approach: the increase in entropy of an isolated system is not due to growing obsolescence of past knowledge of an observer who is using a 'reduced description' or a 'simplified language' to study the system, but rather is a dynamical process undergone by the system. We can clarify this point by studying the following phenomenon that is described in almost every textbook of thermodynamics. We consider a gas in a well-insulated container of fixed volume V. Initially the gas is confined in a region of volume V/2 by means of a partition, and is in equilibrium at pressure P and temperature T. If the partition is removed, the gas fills eventually the whole container, and reaches an equilibrium state at pressure P/2 and temperature T. Using well-established thermodynamic relations we calculate that the value of the entropy at the final state is larger than the value of the entropy at the initial state and that the two states have the same energy. Accordingly, we say that this is an irreversible process. We believe that the increase in the entropy during this phenomenon did not occur in the mind of the observer but has occurred in the system itself. As a strong proof of this argument, we note that the amount of work that can be extracted from the system in conjunction with a reservoir (at temperature T and pressure P/2) has diminished.

2.5.2 Subsystem Dynamics

Extensive efforts have been made to describe the approach to equilibrium in thermodynamics, using subsystem dynamics [Kossakowski, 1972a, b; Lindblad, 1976, Korsch and Steffen, 1987]. Although dynamics of a closed system is represented by a

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unitary transformation, it is argued that the dynamics of a subsystem is not necessarily unitary. According to Lindblad: "It seems that the only possibility of introducing an irreversible behavior in a finite system is to avoid the unitary time development altogether by considering non-Hamiltonian systems. One way of doing this is by postulating an interaction of the considered system S with an external system R like a heat bath or a measuring instrument... If the reservoir R is supposed to be finite (but large) then the time development of the system S+R may be given by a unitary group of transformations. The partial state of S then suffers a time development which is not given by a unitary transformation in general. "

However, this approach is not suitable for our purposes, since in the examples of phenomena presented at the beginning of the chapter, isolated (closed) systems approach equilibrium without interacting with a heat bath or environment. We take the point of view that in these examples, dissipation occurs within the system itself and not at its interface with the environment or at the boundaries. The importance of dissipation in isolated systems has been emphasized by Gyftopoulos and Beretta [1991e], and Park and Simmons [1981].

Park and Simmons [1981] also commented on the subsystem dynamics approach: "... in any bounded mechanical system obeying a unitary law of motion the total entropy is invariant and, since the overall motion is quasiperiodic [Percival, 1961], the entropy of a subsystem ... will also be quasiperiodic and hence exhibit no Second-Law unidirectionality... Thus the Second-Law behavior of A (the system interacting with the environment) is only temporary, and highly dependent upon the choice of an initial condition..."

2.5.3 A New Expression for Entropy

In this approach, irreversible phenomena are treated by invoking special limit procedures or modifying the expression for entropy, but without altering conventional unitary quantum dynamics [Jancel, 1969]. Park and Simmons [1981] expressed their skepticism toward this approach as "entropy may increase indefinitely but only in infinite-volume, infinite-population assemblies. Even if rigorously correct, such propositions can hardly be germane to the physical problem, since realistic systems in which entropy is observed to increase are in fact finite."

In addition, the time evolution implied by the dynamical law of quantum mechanics is reversible [Messiah, 1961; Jancel, 1969], i.e., the initial state of the system can be restored without leaving a net effect on the environment. Hence, if the time evolution of the system is described by the Schrödinger equation, the laws of thermodynamics imply that the value of entropy must remain invariant. Therefore, in conventional quantum mechanics, any expression which increases in time does not represent entropy.

Furthermore, Ochs [1975], Aczel *et al* [1974] have studied extensively the problem of defining a measure of information. The conclusion reached in the studies of Aczel *et al* is that the only "natural" measures of information ("natural" in the sense that they have all the properties expected from a measure of information) are the Shannon entropy I_S (Equation 2.12) and the Hartley entropy I_H given by the relation

$$I_H = k \ \text{Log}\big(N(\rho)\big), \tag{2.13}$$

where $N(\rho)$ is the number of non-zero eigenvalues of ρ. The work of Aczel *et al* is purely information theoretic. Ochs applied the results of this work to statistical quantum mechanics and showed that the only "reasonable measure of the intrinsic dispersion of

quantum states complying with the general ideas of quantum statistics" is given by the von Neumann entropy (Equation 2.11).

2.5.4 A New Dynamical Law

In this section the difficulties encountered in modifying the dynamics of quantum mechanics are studied in detail. The invariance of the von Neumann entropy in a system whose time evolution is described by the Schrödinger equation has led scientists to modify this equation. This seems to be the most promising approach to the problem and hence attracted the attention of many scientists. This is also the remedy proposed by Wehrl [1978].

The first and most important observation is that, as long as thermodynamics is considered as a statistical theory of quantum mechanics, independent of the dynamical law chosen, probabilities assigned to possible states are time invariant. To show this, consider a heterogeneous ensemble E prepared using scheme Π. This ensemble E can always be divided into non-overlapping homogeneous subensembles $\{E_i\}$. Every member of the subensemble E_i is associated with a unique physical state $\{\varepsilon,\psi_i\}$. The statistical state can be expressed as $\{\varepsilon,\rho(t)\}$, where

$$\rho(t) = \sum_i p_i P_i \quad \text{and} \quad P_i = |\psi_i\rangle\langle\psi_i|. \tag{2.14}$$

The time evolution of every element of E is described by the dynamical law of mechanics. Therefore, every system in state $\{\varepsilon,P_i\}$ evolves to a uniquely determined state $\{\varepsilon,P'_i\}$ at a later instant of time t' (causality). Hence the statistical state at t' is $\{\varepsilon,\rho(t')\}$, where

$$\rho(t') = \sum_i p_i P'_i. \tag{2.15}$$

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Combining Equations (2.12) and (2.15) we see that the Shannon entropy remains invariant during the time evolution of the ensemble E. It may be possible to achieve an increase in the value of I_v (Equation (2.11)) by altering the dynamical law of quantum mechanics, but this does not correspond to an increase in the amount of chaos in the ensemble E, since the abundances of different states (the p_i's) remain constant.

There are additional difficulties associated with the modification of the dynamical law of statistical quantum mechanics. It is shown in Appendix A that any modification which maintains the linearity of the equation of motion in ψ implies a unitary time evolution, hence both I_v and I_S are time invariant. Thus all the equations of motion proposed as an alternative to the Schrödinger equation are nonlinear in ψ. As explained in Appendix A, however, if a nonlinear Schrödinger equation is used, the equation of motion of statistical quantum mechanics (similar to Equation (2.10)) becomes ambiguous due to non-unique decomposition of a statistical state into pure states. Furthermore, the nonlinear Schrödinger equations proposed in the literature are not energy preserving and, most of the time, have limited validity. A full review of nonlinear Schrödinger equations is given in Appendix A.

From these observations, we conclude that, within the framework of statistical mechanics, a new dynamical law will not resolve the problem of describing irreversible phenomena.

Chapter 3

3. Non-Statistical Approach

In this chapter we present a non-statistical approach to thermodynamics. This is done in two steps. Implications of the new understanding of thermodynamics are presented in Section 3.1, and the postulates of the new theory, called quantum thermodynamics in Section 3.2.

We believe that a non-statistical approach to thermodynamics is indispensable because the statistical understanding of the theory leads to inconsistencies. Furthermore, the definition of thermodynamics we have adopted in Section 2.1 is compatible only with a non-statistical approach.

3.1 Implications of the Non-Statistical Approach

In this section, we present some general results of thermodynamics in view of the new non-statistical approach. They are discussed in great depth by Gyftopoulos and Beretta [1991].

The theories of mechanics and thermodynamics developed separately and without any explicit relation between the two. Some of the results we present in this section, are obtained in thermodynamics independently of its relation to mechanics, i.e., without any concern whether thermodynamics is a statistical or a non-statistical theory. Nevertheless, they play an important role in the foundations of the newly proposed theory of quantum thermodynamics.

We begin by presenting the statements of the first and second laws of thermodynamics adopted in this dissertation. These laws imply the existence of several

properties of systems. We give the definition of these properties. Next, we describe a convenient and instructive graphical representation of the states of a system - the entropy versus energy graph - which captures many results of thermodynamics.

3.1.1 First and Second Laws of Thermodynamics

We gave the definition of thermodynamics in Section 2.1, and the definitions of the physical constructs necessary for the discussion (system, property, state) in Section 2.2. We give a special name to a change of state of a system that involves no external effects other than the change in elevation of a weight of mass M in a uniform gravitational field of acceleration g. We call it a <u>weight process</u>. The change in the elevation of a weight is equivalent to any mechanical effect. In terms of these concepts, the first law of thermodynamics is stated as follows.

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

A very important consequence of the first law is that every system in any state can be assigned a property that we call energy. For the sake of convenience, we select once and for all a reference state A_0 of the system A and a reference weight with mass M in a uniform gravity field with acceleration g. By virtue of the first law, for a given state A_1 of a system A, there exists a weight process with A_0 and A_1 as end states. We denote by z_0 and z_1 the elevation of the weight when the system is in states A_0 and A_1, respectively. Again by virtue of the first law, the quantity $Mg(z_1-z_0)$ is fixed by the end states. Next, we evaluate the quantity E_1 by means of the relation

$$E_1 = E_0 - Mg(z_1 - z_0)$$ (3.1)

where E_0 is a constant fixed once and for all for system A. It is straightforward to check that Equation (3.1) defines a property E of system A, with value E_1 at any state A_1, that we call energy. It is an additive property provided that the value assigned to the reference state of the composite system is selected consistent with the values assigned to the reference states of its parts.

The statement of the second law of thermodynamics we have adopted is due to Hatsopoulos and Keenan [1965], and has been extended by Gyftopoulos and Beretta [1991f, i]. It includes all correct previous statements of the second law as special cases. We need to make one more definition to give the statement of the second law: A process is reversible if it can be performed in at least one way such that both the system and its environment can be restored to their respective initial states. In Section 2.2.3, we have classified states in terms of their evolution as a function of time. In the light of this classification, the second law introduces the concept of stability of equilibrium to the theory of thermodynamics. Here, for the sake of simplicity, we give a simplified form of the statement of the second law.

Second Law: Among all the states of a system with a given value of energy, and given values of the amounts of constituents and the parameters, there exists one and only one stable equilibrium state. Moreover, starting from any state of a system it is always possible to reach a stable equilibrium state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.

One consequence of the first and the second law is that, starting from a stable equilibrium state of any system, no energy can be transferred to a weight in a weight process in which the values of amounts of constituents and parameters of the system experience no net changes. This consequence is often referred to as the impossibility of a

perpetual-motion machine of the second kind. In some expositions of thermodynamics, it is taken as the statement of the second law. Here, it is only one aspect of the first and second laws.

Among the most important consequences of this law together with the first law of thermodynamics is the existence of properties of systems, such as adiabatic availability, available energy, generalized available energy, and entropy, which are defined for all states.

For example, for a given state A_1 of a system A, there exists a reversible weight process that starts from A_1 and ends in a stable equilibrium state A_0 which shares the same values of amounts of constituents and parameters with A_1. We denote by z_0 and z_1 the elevation of the weight when the system is in states A_0 and A_1, respectively. We evaluate the quantity Ψ_1 by means of the relation

$$\Psi_1 = Mg(z_0 - z_1). \tag{3.2}$$

It is straightforward to check that Equation (3.2) defines a property Ψ of system A, with value Ψ_1 at any state A_1, that we call <u>adiabatic availability</u>. It represents the largest amount of energy that can be transferred to a weight in a weight process without net changes in the values of amounts of constituents and parameters. It admits only non-negative values.

We define an idealized kind of system that provides useful reference states both in theory and in applications. A <u>reservoir R</u> is a system that behaves in a manner approaching the following limiting conditions: i) It passes through stable equilibrium states only; ii) in the course of finite changes of state at constant or varying values of its amounts of constituents and parameters, it remains in mutual stable equilibrium with a duplicate of itself that experiences no such changes; iii) at constant values of the amounts of constituents and the parameters of each of two reservoirs initially in mutual stable

equilibrium, energy can be transferred reversibly from one reservoir to the other with no net effect on any other system.

Given a system A and a reservoir R, each with fixed values of amounts of constituents and parameters, the adiabatic availability of the composite of system A and reservoir R is a property of system A+R called <u>available energy of A with respect to reservoir R</u>. Like energy and adiabatic availability, it is defined for all states of a system. It can be shown that it is an additive property.

Given a reservoir R with fixed values of amounts of constituents and parameters, the state of the composite system A+R, in which the system A is in state A_1 with values of amounts of constituents and parameters $\{n_1, \beta_1\}$ and the reservoir R in state R_1 is denoted by $(AR)_1$. By virtue of the laws of thermodynamics, given a reservoir R, a set of values of amounts of constituents and parameters $\{n_0, \beta_0\}$ and a state A_1, there exists a reversible weight process that starts from $(AR)_1$ and ends in a stable equilibrium state $(AR)_0$ such that A_0 corresponds to $\{n_0, \beta_0\}$, and the reservoir experiences no net change in its values of amounts of constituents and parameters. Again, we denote by z_0 and z_1 the elevation of the weight when the composite system is in states $(AR)_0$ and $(AR)_1$, respectively. We evaluate the quantity Ω_1^R by means of the relation

$$\Omega_1^R = Mg(z_0 - z_1). \tag{3.3}$$

It is straightforward to check that Equation (3.3) defines a property Ω^R of the composite system A+R, with value Ω_1^R at any state $(AR)_1$, that we call <u>generalized available energy</u> of system A with respect to reservoir R and set of values $\{n_0, \beta_0\}$. It can be shown that the difference in generalized availabilities with respect to the same reservoir R and the same values $\{n_0, \beta_0\}$ of any two states A_1 and A_2, denoted by $\Omega_1^R - \Omega_2^R$ is independent of the set of values $\{n_0, \beta_0\}$. The generalized available energy Ω_1^R of system A with respect to reservoir R and values $\{n_0, \beta_0\}$ representes the largest amount of energy that can be

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transferred to a weight out of the composite of a system A and a reservoir R in a weight process that starts with A in state A_1 with values $\{n_1, \beta_1\}$ and ends with A in a state with values $\{n_0, \beta_0\}$, while the reservoir experiences no net change in its values of amounts of constituents and parameters.

Observations of physical phenomena that can be represented as weight processes show that, in general, the amount of energy that can be transferred from the system to the weight differs from the energy of the system above the ground-state energy. In other words, the capacity of a system to raise a weight is not always equal to the energy of the system in excess of the ground-state energy. For example, an initially charged battery can raise a weight via an electric motor. However, left idle and well insulated on a shelf, the battery discharges internally without transferring out any energy, and at the end, it has lost all its capacity to raise a weight via the electric motor. The difference between the energy of a system and its capacity to raise a weight in a weight process is related to the difference between energy and adiabatic availability. Similarly, the difference between the energy of a system and its capacity to raise a weight when in combination with a reservoir is related to the difference between energy and available energy. An alternative and more general way of accounting for these differences is by means of the property called entropy.

For the sake of convenience, we select once and for all a reference state A_0 with values $\{n_0, \beta_0\}$ for system A, an auxiliary reservoir R with fixed values of amounts of constituents and parameters, and an arbitrary set of values $\{n, \beta\}$ of the amounts of the constituents and the parameters for system A. For any state A_1 of system A with values $\{n_1, \beta_1\}$, we evaluate the difference E_1-E_0 between the energies of states A_1 and A_0, and the difference $\Omega_1^R - \Omega_0^R$ between the generalized available energies of the two states with respect to the auxiliary reservoir R and the set of values $\{n, \beta\}$. As explained earlier, each of these differences is measurable by means of an appropriately defined weight process (Equations (3.1) and (3.3)).

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In terms of these differences, we compute the value S_1 using the relation

$$S_1 = S_0 + \frac{1}{c_R} \left[(E_1 - E_0) - \left(\Omega_1^R - \Omega_0^R \right) \right] \tag{3.4}$$

where S_0 is a constant fixed once and for all for system A, and c_R is a well-defined positive constant property of reservoir R.

Because each of the differences E_1-E_0 and $\Omega_1^R - \Omega_0^R$ is independent of the set of values $\{n, \beta\}$, we conclude that S_1-S_0 is independent of these values and that also their role is only auxiliary. Furthermore, the choice of the constant c_R is such that the value S_1 associated with state A_1 is independent of the reservoir used in the set of operations and measurements just cited. In other words, no matter what reservoir is used, we conclude that we always obtain the same values S_1 for the given state A_1 and therefore that the role of the reservoir in these operations and measurements is only auxiliary. Because these conclusions are valid for any state A_1 of system A, Equation (3.4) defines a property S of system A, with value S_1 in any state A_1, that we call <u>entropy</u>.

It can be shown that it is possible to assign absolute values to entropy that are nonnegative. Like energy, entropy is an additive property, i.e., the entropy of a composite system equals the sum of the entropies of the component subsystems, provided that the subsystems are independent of each other. It can be shown that in a reversible weight process for a system A that changes from a state A_1 to a state A_2, the value of the entropy remains unchanged, i.e., $S_2 = S_1$. In an irreversible weight process, however, in which system A changes from a state A_1 to a state A_2, the value of the entropy increases, i.e., $S_2 > S_1$. We know from many experiences that changes of state can occur in isolated systems spontaneously. Because a spontaneous change from a state A_1 to a state A_2 may be regarded as a weight process with null effect on the weight, we conclude that $S_2 = S_1$ if the process is reversible, and $S_2 > S_1$ if the process is reversible. This is known as *the principle of nondecrease of entropy.* Because changes of state cannot occur

instantaneously, we conclude that the principle of nondecrease of entropy is a time dependent result, i.e., a relation between entropy values at two different instants of time for a system that at time t_1 is in state A_1 and at a later instant of time t_2 in state A_2.

3.1.2 Entropy versus Energy Graphs

Because they are defined in terms of the values of the amounts of constituents, the parameters, and a complete set of independent properties, states can in principle be represented by points in a multidimensional geometrical space with one axis for each amount, parameter, and independent property. Such a representation, however, would not be enlightening because the number of independent properties is very large. Nevertheless, useful information can be summarized by first cutting the multidimensional space with a hypersurface corresponding to given values of each of the amounts of constituents and each of the parameters, and then projecting the result onto a two-dimensional plane. Here we consider the entropy S versus energy E plane that illustrates many of the basic concepts in thermodynamics.

We restrict our consideration to a system with volume V as the only parameter. For given values of the amounts of constituents and the volume, we project the multi-dimensional state space of the system onto the S versus E plane. The projection has the shape of the cross-hatched area in Figure 3.1. The curve of the stable equilibrium states is smooth and concave.

By virtue of the second law of thermodynamics, a point on the curve of stable equilibrium states represents one and only one state. For given values of energy, amounts of constituents and volume, the stable equilibrium state has the largest value of entropy than any other state sharing the same given values. In the literature, stable equilibrium states are often called thermodynamic equilibrium states. These are the states studied in thermostatics. Therefore, thermodynamics admits thermostatics as a special case -

maximum-entropy physics. The slope of the curve at each point gives the inverse temperature associated with the corresponding stable equilibrium state.

Each point either inside the cross-hatched area or on the horizontal line S=0 represents a large number of states. They can be any state except a stable equilibrium state. The zero-entropy states correspond to states contemplated in mechanics. Therefore, thermodynamics admits mechanics as a special case as well - zero-entropy physics.
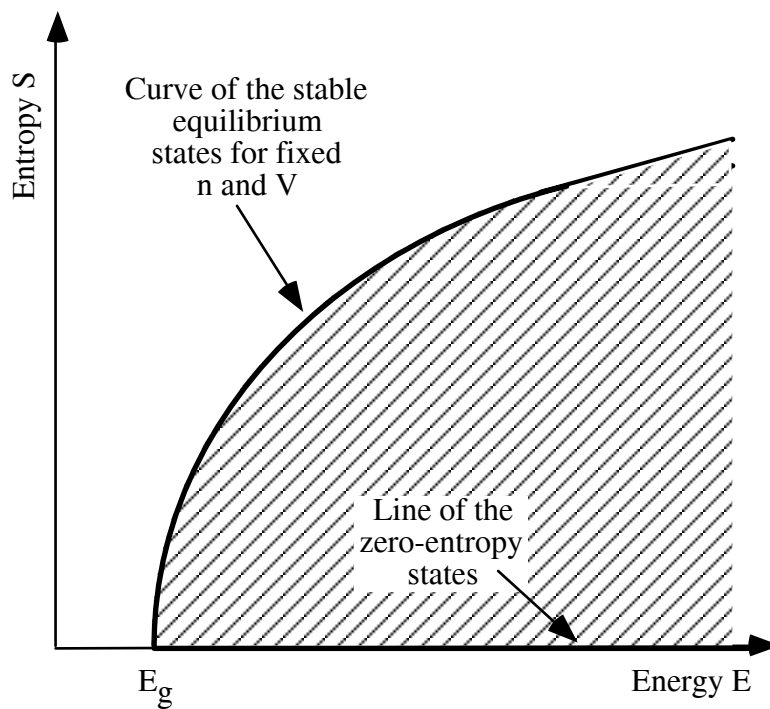

Figure 3.1 Entropy versus energy graph

3.2 Postulates of Quantum Thermodynamics

Here we present the postulates of quantum thermodynamics which encompasses mechanics and thermodynamics within a single mathematical structure [Hatsopoulos and Gyftopoulos, 1976].

Postulate 1.   *Systems*

With every system there is associated a complex, separable Hilbert space H. Denoting the countable infinity by $\aleph_0$, we have either $\dim(H) = \aleph_0$, or $\dim(H) = n = $ finite and then H is equivalent to an n-dimensional complex Euclidean space C^n [Conway, 1985].

The Hilbert space associated with a composite system of two independent subsystems A and B which are associated with Hilbert spaces H_A, H_B, respectively, is the direct product $H_A \otimes H_B$.

This postulate is identical to the first postulate of quantum mechanics presented in Section 2.4.1.

Postulate 2.   *Properties and Observables*

Among the properties associated with a system, there is a special class of them called the <u>observables</u>. They are associated with linear, self-adjoint, closed operators {H,I,J,...} on the Hilbert space H. Using spectral theory, we can express each of these operators in the form:

$$J = \int \lambda\, dE(\lambda), \tag{3.5}$$

where the set $\{\lambda\}$ is the spectrum of J, and $dE(\lambda)$ is a projection-valued measure.

The spectrum of each such operator is non-empty and real. If dim(H)=n, the spectrum of any operator J correponding to an observable is purely point spectrum, and the elements of the spectrum $\{\lambda\}$ are called the eigenvalues of J. If dim(H)= $\aleph_0$, because the residual spectrum of a self-adjoint operator is empty [Rudin, 1973], the spectrum of J can be decomposed into two parts: the point spectrum and the continuous spectrum. It can so happen that either of these two sets is empty, in which case we say that J has purely continuous (or, point) spectrum, respectively. Again, the elements of the point spectrum are called the eigenvalues of J [Conway, 1985].

As explained in Section 2.2.6, upon measurement of a property performed on a system we always get a precise number. If this property is an observable, the measurement result is necessarily in the spectrum of the operator which is associated with that observable. For example, if the operator associated with the observable is J (Equation (3.5)), then the measurement result is in the set $\{\lambda\}$.

An important implication of the superselection rules [Wick *et al*., 1952] is the existence of linear, self-adjoint, closed operators that do not correspond to physical observables. Furthermore, if the dimension of the Hilbert space is $\aleph_0$, some operators that correspond to observables are unbounded, hence they are not continuous. Examples of such operators are the Hamiltonian, the position and the linear momentum operators. All the linear operators on a finite-dimensional Hilbert space are bounded, hence continuous [Conway, 1985; Rudin, 1973].

Although in conventional quantum mechanics properties other than observables do not play an essential role, they are indispensable in thermodynamic thinking. Entropy and adiabatic availability [Gyftopoulos and Beretta, 1991g, h] are examples of such properties. The mathematical representatives of some of these properties remain to be discovered. For example, in Chapter 4, we search for the mathematical representative of entropy.

Postulate 3.   *State*

As described in Section 2.2, at each instant of time, to every system prepared according to a preparation scheme Π that generates a homogeneous ensemble E, there corresponds a state. In quantum thermodynamics, the state is the set ε of instantaneous expressions corresponding to independent properties and a self-adjoint, non-negative definite, unit-trace operator ρ on the Hilbert space H, called the density operator. If two systems A and B are independent, and the state of A is $\{\varepsilon_A, \rho_A\}$, and the state of B $\{\varepsilon_B, \rho_B\}$, then the state of the composite system A+B is $\{\varepsilon_A \cup \varepsilon_B, \rho_A \otimes \rho_B\}$.

Because it is trace-class, the density operator ρ is also compact [Conway, 1985]. Hence, its spectrum is purely a point spectrum: $\{p_i\}$. The eigenvalues $\{p_i\}$ are non-negative, the degeneracy of a positive eigenvalue p_i is finite, and the only possible accumulation point of the spectrum of ρ is 0. Furthermore, there exists an orthonormal basis $\{\psi_i\}$ in H such that

$$\rho \psi_i = p_i \psi_i. \tag{3.6}$$

The set of states in quantum thermodynamics is broader that the set of states in quantum mechanics. The former admits states $\{\varepsilon, \rho\}$ for which either $\rho^2 = \rho$ or $\rho^2 \neq \rho$, whereas the latter is restricted only to states $\{\varepsilon, \rho\}$ for which $\rho^2 = \rho$, i.e., ρ is a projection. The broad set of states of quantum thermodynamics was first introduced by Hatsopoulos and Gyftopoulos [1976], and then adopted by Park and Simmons [1981], and Beretta *et al* [1984, 1985].

Independent of the work of Hatsopoulos and Gyftopoulos, Jauch [1968] used the set of density operators (including $\rho \neq \rho^2$) to describe states (note that his definition of state does not include the set of instantaneous expressions corresponding to independent observalbles). However, Jauch did not investigate the problem of describing quantum irreversible phenomena. He postulated that the dynamical law of quantum mechanics is

given by the von Neumann equation (Equation 2.10)., and showed that it implies a reversible time evolution.

Messer and Baumgartner [1978] used the set of density operators (including $\rho \neq \rho^2$) to describe states (they did not include the set of instantaneous operators in their definition of state either), and studied different modified von Neumann equations to describe quantum dissipative phenomena. We will review their work in greater depth in Chapter 5 where we investigate the dynamical aspects of quantum thermodynamics.

It is noteworthy that the mathematical representation of the density operator in quantum thermodynamics is identical to that of the statistical state operator in statistical quantum mechanics. However, the physical meaning of the former is fundamentally different from that of the latter. The former is associated with a state of the system, whereas, the latter is a probability distribution over a large member of presumed states of the system, each described by a projection operator. A helpful way of visualizing this difference is by means of ensembles. In thermodynamics, a set ε and a density operator ρ represent the state of a member of a homogeneous ensemble. In statistical quantum mechanics, the statistical operator represents probabilities associated with different members of a heterogeneous ensemble. The difference between the physical meanings of a density operator and a statistical operator and criteria for its experimental verification were first recognized by Hatsopoulos and Gyftopoulos [1976], and has been emphasized by Park [1988]. It has also been discussed by Messer and Baumgartner [1978]. This recognition is a clear indication of the conceptual distinction between quantum thermodynamics which is a non-statistical quantal description of thermodynamics, and statistical quantum mechanics which is a statistical expansion of quantum mechanics.

If a measurement of an observable is performed on a system in state $\{\varepsilon,\rho\}$, and the operator associated with the observable is J (Equation (3.1)), the probability of getting a measurement result between j and j+dj is

$$\sum_i p_i \int_j^{j+dj} \lambda \langle \psi_i, dE(\lambda)\psi_i \rangle = \sum_i p_i \int_j^{j+dj} \lambda dE_{\psi_i}(\lambda). \tag{3.7}$$

This implies that the arithmetic mean value <J> of the data yielded by measurements of the observable on the homogeneous ensemble E is given by the inner product or, alternatively, by the trace operation

$$\langle J \rangle = \sum_i p_i \langle \psi_i, J\psi_i \rangle = \mathrm{Tr}(J\rho). \tag{3.8}$$

As mentioned earlier, properties other than observables play an essential role in quantum thermodynamics and may be included in the set ε. For example, entropy, adiabatic availability (which are defined for all states) and temperature (which is defined for stable equilibrium states only) are not observables in the quantum-theoretic sense and yet they are properties of the system. What we mean by the last statement is that there exists no linear, closed, self-adjoint operator J on H such that the measurement results of a property which is not a quantum observable can be given by Equation (3.7). Therefore, in general, the value of such a property cannot be expressed in the form of Equation (3.8). In Chapter 4, we show that the expression for (the value of) entropy is

$$\langle S \rangle = -k \ \mathrm{Tr}(\rho \ \mathrm{Log}(\rho)), \tag{3.9}$$

which differs from Equation (3.8) because it is nonlinear in ρ.

At first glance, it is not clear whether the uncertainty relations established in conventional quantum mechanics are also valid in quantum thermodynamics, because the latter involves a broader set of states than the former. Jauch [1963] studied the problem and showed the uncertainty relations apply without any modification even when the set of density operators are not restricted to projections.

Postulate 4.   *Time Evolution*

Because quantum thermodynamics admits quantum mechanics as a special case, the time evolution of a density operator corresponding to a mechanical state ,i.e., $\{\varepsilon,\rho\}$ with ρ a projection ($\rho = \rho^2$) obeys the Schrödinger equation (Equation (2.6)) or, equivalently, the von Neumann equation (Equation 2.10)).

However, the generalized dynamical law of quantum thermodynamics, valid for all states and not only for mechanical states, remains to be established. A few attempts have been made to discover the equation of motion. They are discussed in Chapter 5.

Chapter 4

4. The Expression for Entropy

Because entropy is a well-defined property in thermodynamics [Gyftopoulos and Beretta, 1991g], the question arises "what is the mathematical expression for entropy in the framework of quantum thermodynamics?" To answer this question, in Section 4.1 we state a set of conditions that need to be satisfied by the expression for entropy in quantum thermodynamics, in Section 4.2 we review many expressions that have been proposed in the literature, and in Section 4.3 we use the criteria to decide which expression is acceptable. It turns out that only one expression passes this test which is performed for the first time in quantum thermodynamics. Thus, we conclude that the expression for entropy in quantum thermodynamics is given by Equation (3.9). We end this chapter by presenting, in Section 4.4, certain mathematical conditions imposed on the Hamiltonian operator of a system by the expression for entropy. These conditions are specified for the first time in quantum thermodynamics.

4.1 Conditions to be Satisfied by the Expression for Entropy

In this section, we state a number of conditions that are obtained from general considerations of thermodynamics (presented in Section 3.1), and that must be satisfied by any expression that purports to represent entropy.

1. In contrast to some approaches presented in the literature, where entropy is assigned only to an equilibrium state of large systems, in quantum thermodynamics, a value of entropy is assigned to every state, equilibrium or not, of any system, large or

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small. Therefore, the expression for entropy has to be well-defined in every state of every system.

2. The value of entropy should remain invariant in a reversible adiabatic process and increase in an irreversible adiabatic process. More specifically, if the time evolution of the density operator obeys the von Neumann equation (Equation (2.10)), the expression should assign the same value of entropy at any instant of time because the process described by this equation is a reversible adiabatic process [Jauch, 1963].

3. Entropy is an additive property, i.e., the entropy of a composite system equals the sum of the entropies of the parts of the system, provided that they are independent of each other.

4. The value of entropy in any state is non-negative, and vanishes only in mechanical states.

5. For given values of energy, amounts of constituents, and parameters, one and only one state should correspond to the largest value of entropy.

6. The curve of stable equilibrium states on the entropy versus energy graph should be concave and smooth.

7. If we denote a stable equilibrium state of a composite of two independent systems A and B by $\{\varepsilon_A \cup \varepsilon_B, \rho_{AB} = \rho_A \otimes \rho_B\}$, where $\{\varepsilon_A, \rho_A\}$ and $\{\varepsilon_B, \rho_B\}$ are the stable equilibrium states of the subsystems A and B, the entropy expression should be such that the entropy maximization procedure used to establish the stable equilibrium states yields identical temperatures, and total potentials for the three systems -composite, A, and B.

8. For stable equilibrium states, the expression for entropy in quantum thermodynamics should reduce to the relations that have been established experimentally and that express entropy in terms of the values of energy, the amounts of constituents and the parameters.

4.2 Candidate Expressions

In the literature many mathematical expressions have been proposed for entropy. Aczel *et al* [1974], Ochs [1975], and Wehrl [1978] gave a review of these expressions. Some of these expressions are as follows:

the von Neumann entropy (Equation (2.11))

$$I_v = -k \; Tr\big(\rho \; Log(\rho)\big); \tag{4.1}$$

the Hartley entropy (Equation (2.13))

$$I_H = k \; Log\big(N(\rho)\big), \tag{4.2}$$

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

the Daróczy entropy of degree β

$$I_\beta = \frac{1}{2^{1-\beta}-1}\big(Tr(\rho)^\beta - 1\big); \tag{4.3}$$

where $\beta > 0, \; \beta \neq 1$;

the Rényi entropy of order α

$$I_\alpha = \frac{k}{1-\alpha} Log\big(Tr\big(\rho^\alpha\big)\big); \tag{4.4}$$

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

the infinite norm entropy

$$I_\infty = -k \; Log\|\rho\|_\infty; \tag{4.5}$$

where $\left\|\rho\right\|_{\infty} = p_{max}$ is the largest eigenvalue of ρ;

the Tolman entropy

$$I_T = -k \sum_i \rho_{ii} \text{Log}(\rho_{ii}), \qquad (4.6)$$

where ρ_{ii} is the diagonal element of ρ in energy representation;

and the coarse-grained entropy [Tolman, 1938; Jancel, 1969]

$$I_c = -k \sum_i P_i \text{Log}(P_i), \qquad (4.7)$$

where P_i's are the "coarse-grained probabilities" defined by Tolman [1938].

Other expressions of entropy have appeared in the literature. They are not included here, because it is evident from their mathematical structure that they violate many of the conditions stated in Section 4.1.

4.3 The Expression for Entropy

In this section, we examine which of the expressions for entropy given in Section 4.2 meet the requirements summarized in Section 4.1. Upon investigation, we conclude that only the von Neumann entropy conforms with all the conditions.

All the expressions included in Section 4.2 are defined for all states and, therefore, satisfy Condition 1.

The coarse-grained entropy (Equation (4.7)) increases when the time evolution of the system obeys the von Neumann equation (Equation (2.10)) [Jancel, 1969], hence violates Condition 2.

The Tolman entropy (Equation (4.6)) does not assign the same value of entropy to every mechanical state. But von Neumann [1955] has shown that any two mechanical states can be connected by means of a reversible adiabatic process. Hence all these states must have the same value of entropy. Therefore, we reject the Tolman entropy because it violates Condition 2.

The Daróczy entropy of degree β (Equation 4.3) is not additive [Ochs, 1975], i.e., it does not satisfy Condition 3. Accordingly, the Daróczy entropy must be rejected.

It is easy to verify that all the expressions we have not rejected so far satisfy Condition 4. In Appendix B, we show that the Hartley entropy (Equation (4.2)) violates Condition 5, and the infinite norm entropy (Equation (4.5)) Condition 6. So the Hartley and infinite norm entropies are rejected.

Katz [1967] has shown that the von Neumann entropy (Equation (4.1)) satisfies Condition 5, and that the stable equilibrium state of a petit system then has the form $\{\varepsilon, \rho_\beta\}$, with

$$\rho_\beta = \frac{\exp(-\beta H)}{\mathrm{Tr}(\exp(-\beta H))}, \quad \beta = \frac{1}{kT} \tag{4.8}$$

where T is temperature at that state, and H the Hamiltonian operator. In Appendix B, we show that the von Neumann entropy also satisfies Conditions 6 and 7.

Again in Appendix B, we show that the Rényi entropy of degree α (Equation (4.4)) satisfies Condition 5, and that the density operator of a stable equilibrium state of a petit system is of the form

$$\rho_\gamma = (\lambda + \gamma H)^{1/(\alpha-1)} \tag{4.9}$$

where, λ and γ are real numbers. In Appendix B, we show also that, for $0<\alpha<1$, the Rényi entropy satisfies Condition 6 but not Condition 7. Accordingly, the Rényi entropy is not acceptable.

Therefore, we conclude that among the expressions proposed in Section (4.1) only the von Neumann entropy satisfies Conditions 1 to 7. As mentioned earlier, the similarity in the mathematical structure of statistical quantum mechanics and quantum thermodynamics implies that the success of the former theory in describing the properties of stable equilibrium states carries over to the latter. Hence, the von Neumann entropy satisfies Condition 8 as well.

In statistical quantum mechanics, several different derivations of the expression for entropy (Equation (2.11)) have been given [von Neumann, 1955; Ochs, 1975]. These derivations are based on a set of axioms. The similarity between the mathematical structures of statistical quantum mechanics and quantum thermodynamics suggests that these derivations can also be used to determine the expression for entropy in the latter theory. Unfortunately, the set of conditions specified in Section 4.1 do not justify all the axioms needed for the derivations. For example, the derivation of the expression for entropy by von Neumann is based on the notion of mixing of pure states, which cannot be justified in quantum thermodynamics.

In the derivation of Ochs which is based on a previous work by Aczel *et al* [1974], the assumptions (the axioms) that the expression for entropy has the "partial isometric invariance" and "subadditivity" features cannot be justified by general considerations of thermodynamics. Their justification in statistical quantum mechanics makes extensive use of the meaning ad hoc assigned to entropy as "the intrinsic measure of the dispersion of quantum states".

The only attempt to establish the expression for entropy in quantum thermodynamics has been done by Hatsopoulos and Gyftopoulos [1976]. They conclude that the von Neumann entropy is the only expression acceptable in quantum

thermodynamics. However, their derivation contained unnecessary assumptions that are not listed among the conditions presented in Section 4.1. Therefore, this is the first time that the von Neumann entropy is rigorously shown to be the entropy of quantum thermodynamics.

4.4 Implications of the Expression for Entropy

The density operator ρ_β given by Equation (4.8), called the canonical distribution, is well-defined if and only if $\text{Tr}(\exp(-\beta H)) < \infty$. The same condition is valid for density operators established by Katz, and introduced by Gibbs under the name of grand canonical distributions. To the best of our knowledge, systems other than spin systems are described in terms of the concept of position in ordinary space, and conform to the Heisenberg uncertainty principle $(\Delta x)(\Delta p) \geq \hbar / 2$. Both the position operator (which admits a continuous spectrum) and the Heisenberg uncertainty principle require that the Hilbert space H associated with the system has countable infinite dimension, i.e., $\dim(H) = \aleph_0$ [Rudin, 1973; Artin, 1989]. Furthermore, it is experimentally established that these systems admit only positive values of temperatures in stable equilibrium states (i.e., $\beta > 0$).

Therefore, if $\dim(H) = \aleph_0$, the Hamiltonian oprator H must satisfy the condition that $\text{Tr}(\exp(-\beta H)) < \infty$, for some value of $\beta > 0$, i.e., $\exp(-\beta H)$ is of trace-class. Immediate implications of this condition are that: if $\dim(H) = \aleph_0$, (i) the spectrum of H must be purely point spectrum, i.e., H is diagonalizable; (ii) the Hamiltonian is unbounded, yet bounded from below, i.e., there exists a smallest eigenvalue of H, called the ground state energy; (iii) the spectrum of H contains no accumulation point; and (iv) the degeneracy of any eigenvalue of H is finite. Because it is unbounded, the Hamiltonian operator H is also discontinuous [Conway, 1985].

In quantum mechanics, there are well-known examples of systems which violate the requirement that $Tr(\exp(-\beta H)) < \infty$, for some value of $\beta > 0$: the free particle because its Hamiltonian has purely continuous spectrum, and the hydrogen atom because its energy eigenvalues converge to 0, i.e., there exists an accumulation point in the spectrum of H. We can explain these discrepancies by recognizing that no particle is free in nature, i.e., both the so-called free particle, and the hydrogen atom are actually confined in a finite volume. Because the volume is finite, if we use the Wentzel-Kramers-Brillouin (WKB) approximation we find that the energy eigenvalues are discrete and unbounded. However, both the free particle and hydrogen atom examples are extremely useful and valuable in quantum physics. The free particle helps us understand the time evolution of a loosely held particle, and the hydrogen atom problem provides an excellent numerical approximation for energy eigenvalues that are not close to zero.

It is noteworthy that the restriction $Tr(\exp(-\beta H)) < \infty$ is also necessary in statistical quantum mechanics, because of the identical mathematical representations of ρ and the von Neumann entropy (Equation (2.11)).

We would like to emphasize that the restriction imposed on the Hamiltonian operator H cannot be interpreted as a deficiency of the von Neumann entropy, because any expression which is solely a function of the eigenvalues of the density operator, and satisfies Conditions 3 and 6 requires the same restriction. To show this we consider a system such that dim(H)=n, then an acceptable density operator according to the third postulate of quantum thermodynamics is given by the relation

$$\rho_n = \frac{1}{n} I_n, \tag{4.10}$$

where I_n is the identity operator on H. The eigenvalues $\{p_i\}$ of such a ρ_n are all identical and equal to 1/n. Hence the entropy of the state $\{\varepsilon, \rho_n\}$ is a function of n only, i.e., $S(\rho_n) = f(n)$. Using the additivity of entropy (Condition 3) we find

$$S(\rho_{nm}) = S(\rho_n \otimes \rho_m) = S(\rho_n) + S(\rho_m). \tag{4.11}$$

or, equivalently

$$f(nm) = f(n) + f(m). \tag{4.12}$$

It is easy to show that the only smooth function f(n) that satisfies Equation (4.12) is

$$f(n) = k \ \mathrm{Log}(n). \tag{4.13}$$

When the dimension of the Hilbert space is infinite, n goes to infinite, and we conclude that there exists a state with infinite entropy. This state cannot have a finite value of energy. If it did, the concavity of the stable equilibrium states on the S versus E graph (Condition 6) would imply that all the stable equilibrium states have infinite entropy, an implication that is at variance with innumerable experiences. Therefore, we conclude that the Hamiltonian is unbounded, and that its spectrum contains no accumulation point. To the best of our knowledge, this is the first time such a restriction is imposed on the Hamiltonian in quantum thermodynamics.

Chapter 5

5. Dynamics

The power of a physical theory is in its ability to make predictions. In quantum thermodynamics, the time evolution of systems are described by the equation of motion which remains to be discovered. Nevertheless, several features of this equation are known. In this chapter, we investigate the dynamical aspect of quantum thermodynamics. We present the conditions that need to be satisfied by the equation of motion in Section 5.1, and proposed equations of motion of quantum thermodynamics in Section 5.2. Upon investigating the proposed equations in Section 5.3, we conclude that only one suggested by Beretta satisfies all the stated conditions. In Section 5.4, for the first time, we present a special class of solutions of the Beretta equation which plays an important role in describing relaxation phenomena.

5.1 Conditions Imposed on the Equation of Motion

As discussed in Section 3.2, in quantum thermodynamics the state is represented by the set ε of instantaneous expressions corresponding to properties and the density operator ρ. Therefore, in dynamics, we have to describe the time evolution of both the set ε and the density operator ρ. In isolated systems, the set ε is time invariant, and so all we need to describe is the time evolution of ρ. This is done by establishing an equation which governs the evolution of ρ. We call it the equation of motion of quantum thermodynamics.

If system A is not isolated, we need to describe the evolution of the set ε_A as well. One possible approach is to study the behavior of the isolated composite system A+B,

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where B is the union of all systems interacting with the system A. Then, the set ε_{AB} is time independent, and the time evolution of the density operator ρ_{AB} of the composite system is determined by the equation of motion for the composite system. In principle, the set ε_A and the density operator ρ_A at any instant of time t, can be recovered from the state $\{\varepsilon_{AB},\rho_{AB}\}$ of the composite at time t, provided that A is an identifiable subsystem of the composite system.

As mentioned in Section 3.2, the dynamical law (postulate 4) of quantum thermodynamics remains to be established. Nevertheless, we can determine several mathematical conditions that need to be satisfied by the equation of motion.

As a first condition, we believe that the equation of motion should be compatible with the principle of determinism, i.e., without any ambiguity it should allow us to determine the state at any instant of time, given the state at some specific time. The simplest form of equation possessing this feature has the mathematical representation:

$$\frac{\partial \rho}{\partial t} = F(\varepsilon,\rho), \tag{5.1}$$

where $F(\varepsilon,\rho)$ is a linear operator on H which is a function of the state $\{\varepsilon,\rho\}$ and remains to be discovered. Note that the forms of the equations of motion of both classical and quantum mechanics are identical to that of Equation (5.1).

To be an acceptable equation of motion in the framework of quantum thermodynamics, the following mathematical conditions must be satisfied by Equation (5.1).

1. The equation of motion must preserve the Hermiticity of ρ. Accordingly, $F(\varepsilon,\rho)=F^*(\varepsilon,\rho)$, where $F^*(\varepsilon,\rho)$ denotes the adjoint of the operator $F(\varepsilon,\rho)$.

2. The equation must preserve the trace of ρ, i.e., $Tr(\rho)=1$ at any instant of time t. Accordingly, $\dfrac{d}{dt}Tr(\rho)= 0 = Tr(F(\varepsilon,\rho))$.

3. In an isolated system, energy must be conserved, i.e., $\dfrac{d}{dt}\langle H\rangle = 0$, where H is the Hamiltonian operator of the system. Accordingly, $\mathrm{Tr}(HF(\varepsilon,\rho))=0$.

4. The entropy of an isolated system must not decrease, i.e., $\dfrac{d}{dt}\langle S\rangle = -k\ \mathrm{Tr}\big(\mathrm{Log}(\rho)F(\varepsilon,\rho)\big)\geq 0$. Furthermore, there must exist a class of states for which the inequality becomes strict, i.e., the entropy increases, so that the equation can describe irreversible spontaneous processes which are part of our experiences.

5. The equation should preserve the non-negative definiteness of ρ.

6. The equation of motion should reduce to the von Neumann equation (Equation (2.10)) or, equivalently, to the Schrödinger equation (Equation (2.6)) when ρ is a projection ($\rho^2=\rho$), because quantum mechanics is a special case of quantum thermodynamics.

7. Solutions of the equation of motion for a composite of two independent systems A and B should be compatible with the two equations of motion for the parts A and B. If $\rho_{AB}(t)$ denotes the solution of the equation for the composite system for the initial condition $\rho_{AB}(0)=\rho_A(0)\otimes\rho_B(0)$, $\rho_A(t)$ and $\rho_B(t)$ denote the solutions for the initial conditions $\rho_A(0)$ and $\rho_B(0)$, respectively, then we must have $\rho_{AB}(t)=\rho_A(t)\otimes\rho_B(t)$. This condition implies that the operator $F(\varepsilon,\rho)$ of Equation (5.1) satisfies the relation: $F_{AB}(\varepsilon_{AB},\rho_{AB})=F_A(\varepsilon_A,\rho_A)\otimes\rho_B+\rho_A\otimes F_B(\varepsilon_B,\rho_B)$.

8. The solution of Equation (5.1) must exist and be unique for any initial condition $\rho(0)$.

9. The time evolution predicted by the equation of motion must be consistent with experimental observations. Actually, this is the only way the equation of motion of any physical theory can be and is validated.

5.2 Candidate Equations

Though many attempts have been made to establish equations that describe quantum dissipative phenomena within the framework of statistical quantum mechanics, only a few equations of motion have been proposed for quantum thermodynamics. In the former category are the nonlinear Schrödinger equations which are discussed in Section 2.5.4 and are shown to be deficient. Accordingly, in this section we present only the equations of motion proposed for the density operator ρ.

The first equation of motion proposed for the density operator ρ is the von Neumann equation (Equation 2.10) [1955]

$$ i\hbar\frac{\partial\rho}{\partial t} = [H,\rho]. \tag{5.2} $$

In this equation, however, ρ is interpreted as a statistical operator. Only Jauch [1968] considered all density operators $\rho=\rho^2$ and $\rho\neq\rho^2$, and postulated that the dynamical law of his generalized quantum mechanics is given by the von Neumann equation. Later, Hatsopoulos and Gyftopoulos [1976] postulated that the von Neumann equation applies to all density operators, $\rho=\rho^2$ and $\rho\neq\rho^2$, but only for unitary changes of ρ.

In the literature there are attempts to describe quantum dissipative phenomena used subsystem dynamics (Section 2.5.2). For example, several equations of motion for the statistical operator of the subsystem have been developed by Kossakowski [1973], Lindblad [1976], and Gorini *et al* [1976]. These equations are based on the notion of a quantum dynamical semi-group, are derived by using the concept of "complete positivity" [Lindblad, 1976; Gorini *et al*, 1976], and are linear in ρ. They are all of the form

$$ \frac{\partial\rho}{\partial t} = L\rho, \tag{5.3} $$

where L is a linear operator on $L^1(H)$, that is the Banach space over the field of real numbers of self-adjoint trace class linear operators on H. The operator L is sometimes referred to as a super-operator. Because of its similarity with the Liouville equation of classical mechanics, Equation (5.3) is commonly referred to as the "Liouville equation".

Kossakowski's proposal is exclusively for a two-level system, and that of Gorini *et al* applies to systems associated with a finite dimensional Hilbert space. The equation proposed by Lindblad is valid for all systems, and reduces to the equations proposed by Kossakowski and Gorini *et al*. Therefore, in this dissertation, we investigate only the equation of motion proposed by Lindblad [1976]. He considered a super-operator L such that

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] + \sum_n \left(V_n \rho V_n^* - \frac{1}{2}\left\{ V_n^* V_n, \rho \right\}_+ \right) \tag{5.4}$$

where $\left\{ V_n^* V_n, \rho \right\}_+ = V_n^* V_n \rho + \rho V_n^* V_n$, and $\{V_n\}$ are bounded linear operators on H. In the following section, we investigate if this equation of motion is suitable for quantum thermodynamics, interpreting ρ as a density operator rather than a statistical operator.

Messer and Baumgartner [1978] proposed two different equations of motion for the density operator, both nonlinear in ρ (see also Section 3.2). The most important aspect of their work is the recognition that ρ cannot represent a statistical operator. They proposed these equations as a generalization of the nonlinear Schrödinger equations (A.14) and (A.17)) which are valid only for pure states.

The first equation is a generalization of Equation (A.14), and is given by

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] - \frac{1}{2}\gamma\left(V(\rho)\sqrt{\rho} + \sqrt{\rho}V(\rho) \right), \tag{5.5}$$

where γ is a positive constant, and $V(\rho)$ a linear operator such that

$$V(\rho)_{xy} = \left(\sqrt{\rho}\right)_{xy} \mathrm{Log} \frac{\left(\sqrt{\rho}\right)_{xy}}{\left(\sqrt{\rho}\right)_{yx}}, \qquad (5.6)$$

and A_{xy} denotes the "kernel" of the operator A with respect to positions x and y. The kernel of an operator A is given by the inner product $<\delta_x|A|\delta_y>$, where δ_x and δ_y are Dirac delta functions singular at x and y, respectively.

The second equation of motion proposed by Messer and Baumgartner is a generalization of Equation (A.17) and is given by

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho] - \gamma\langle p\rangle[x,\rho], \qquad (5.7)$$

where γ is a positive constant, and x and p are the position and momentum operators, respectively.

Park and Simmons [1981] adopted the generalized set of density operators of quantum thermodynamics, and proposed the nonlinear equation of motion given by

$$\frac{\partial\rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] + \frac{1}{\lambda}\left(\hat{\rho}(\rho) - \rho\right), \qquad (5.8)$$

where $\lambda > 0$, and $\hat{\rho}(\rho)$ is the stable equilibrium state which shares the same values of energy, amounts of constituents and parameters with ρ.

Beretta *et al* [1984] proposed another nonlinear equation for ρ. To express the Beretta equation in a compact form, we introduce the semi-inner product

$$(A,B) = \mathrm{Tr}\left(A^* B\rho\right) - \mathrm{Tr}\left(A^*\rho\right)\mathrm{Tr}(B\rho) = \left\langle A^* B\right\rangle - \left\langle A^*\right\rangle\left\langle B\right\rangle, \qquad (5.9)$$

where A and B are linear, closed operators on H, and define a new operator $\Sigma = -Log(\rho)$ with the convention $Log(0)=0$ which allows us to express the entropy of the system in state ρ as

$$S(\rho) = \langle S \rangle = -k \ Tr(\rho \ Log(\rho)) = k \langle \Sigma \rangle . \tag{5.10}$$

The Beretta equation reads: To every system there corresponds a set $\left\{G_j\right\}$ of n linear, closed, self-adjoint, commuting operators on H, called the generators of motion, such that

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] + \frac{1}{2\tau}\left\{\rho, D(\rho)\right\}_+ \tag{5.11}$$

$$D(\rho) = \frac{\begin{vmatrix} \Sigma - \langle \Sigma \rangle & G_1 - \langle G_1 \rangle & ... & G_n - \langle G_n \rangle \\ (G_1,\Sigma) & (G_1,G_1) & ... & (G_1,G_n) \\ ... & ... & ... & ... \\ (G_n,\Sigma) & (G_n,G_1) & ... & (G_n,G_n) \end{vmatrix}}{\begin{vmatrix} (G_1,G_1) & ... & (G_1,G_n) \\ ... & ... & ... \\ (G_n,G_1) & ... & (G_n,G_n) \end{vmatrix}} . \tag{5.12a}$$

where τ is a positive constant, and $\{\rho,D(\rho)\}_+=\rho D(\rho)+D(\rho)\rho$.

Because it always contains the Hamiltonian, the set $\{G_j\}$ is not empty. The cardinality of the set $\{G_j\}$ depends on the system. In grand systems, i.e., systems which admit fractional expectation values of the amounts of constituents, the number of constituent operators $\{N_i\}$ are also included in the set $\{G_j\}$. Furthermore, the elements of the set $\{G_j\}$ are always linearly independent. For certain systems, the set $\{G_j\}$ contains only the Hamiltonian and Equation (5.12a) reduces to

$$D(\rho) = \frac{\begin{vmatrix} \Sigma - \langle \Sigma \rangle & H - \langle H \rangle \\ (H, \Sigma) & (H, H) \end{vmatrix}}{\left| (H, H) \right|} \, .$$ (5.12b)

The Beretta equation we have just presented applies only to systems which contain one type of constituent. For more than one constituent, Beretta has proposed a more general equation [Beretta *et al*, 1985]. In the generalized form of the Beretta equation, to every constituent n_i of the system, there corresponds a different time constant τ_i. In this dissertation, we assume that all time constants τ_i are identical, in which case the generalized Beretta equation reduces to Equation (5.11).

For certain states the denominator in Equation (5.12a) can vanish and the equation becomes undetermined. For those states, Beretta [1985a] postulated that $D(\rho)$ itself vanishes hence the equation reduces to the von Neumann equation.

Finally, Korsch and Steffen [1987] proposed a nonlinear equation of motion for the statistical operator ρ. The authors recognized the difficulties in interpreting the meaning assigned to ρ, induced by the nonlinearity of the equation. However, they did not state as explicitly as Messer and Baumgartner [1978] that ρ cannot be a statistical operator. The motivation behind the work of Korsch and Steffen is to describe irreversible dissipative time evolution of a system in contact with its environment (an open system). Their equation of motion is given by

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho] + \gamma \Delta(\rho)$$ (5.13)

where $\Delta(\rho)$ is a nonlinear function of ρ given by

either $\quad \Delta(\rho) = (\Sigma - \langle \Sigma \rangle)\rho$ (5.14a)

or $\quad \Delta(\rho) = \dfrac{1}{2}\{A,\rho\}_+ - \langle A\rangle\rho$ $\qquad\qquad\qquad\qquad$ (5.14b)

or a combination of Equations 5.14a and 5.14b, where A is an operator corresponding to an additive property of the system, and $\{A\rho,\rho A\}_+ = A\rho + \rho A$.

5.3 The Equation of Motion

In this section, we examine which of the equations of motion given in Section 5.2 meet the requirements summarized in Section 5.1. Upon investigation, we conclude that only the Beretta equation conforms with all the conditions.

First, we observe that the von Neumann equation (Equation (5.2)) satisfies all the Conditions 1 to 3, and 5 to 8. However, because it implies a unitary transformation in time, the von Neumann equation conserves the value of entropy and violates Condition 4. Accordingly, we conclude that the von Neumann equation is not acceptable.

The two equations of motion proposed by Messer and Baumgartner, Equations (5.5) and (5.7), satisfy Conditions 1 and 2. However, they do not conserve the value of energy, hence violate Condition 3. Even though this last statement alone shows that the equations proposed by Messer and Baumgartner are unacceptable, for the sake of completeness, we investigate them further. The authors also emphasized that the question of whether or not these equations satisfy Conditions 5 and 8 is an open one. Both equations violate Condition 6, however. They are invented in such a way that, when ρ is a projection, they reduce to the nonlinear Schrödinger equations instead of the Schrödinger equation. The exact forms of these nonlinear Schrödinger equations are given in Appendix A. More specifically, Equation (5.5) reduces to Equation (A.14), and Equation (5.7) reduces to Equation (A.17) with c=0. Furthermore, it is not known whether or not Equation (5.5) satisfies Condition 4. It is easy to show that Equation (5.7)

conserves the value of entropy, and therefore violates Condition 4. Based on these observations, we conclude that both equations proposed by Messer and Baumgartner are not acceptable.

Simmons and Park [1981a, b] have criticized the way the Liouville equations are derived for the statistical operator. Here, we are not interested in how the equations are derived, but rather in whether they satisfy Conditions 1 to 9. It turns out that the Liouville equations do not satisfy these conditions.

If it were possible to find a Liouville equation that satisfies the Conditions 1 to 9, we could have postulated it as being the equation of motion of quantum thermodynamics by interpreting ρ as a density operator. This approach would have been fundamentally different from those of Lindblad, Kossakowski and Gorini who "derived" rather than "postulated" their equation. It is noteworthy, however, that if the equation of motion cannot be derived from known principles because these principles do not regularize all experiences, then it must be postulated.

It is easy to verify that the Lindblad equation satisfies Conditions 1 and 2. The first difficulty encountered with the Liouville equations proposed in the literature is that, in general, they are not energy conserving and do not conform with the principle of entropy non-decrease [Park and Simmons, 1981; Simmons and Park, 1981b]. In Appendix C, however, we give a version of the Lindblad equation (Equation (5.4)) which is both energy conserving and entropy non-decreasing, for the special case of a two-level system. Therefore, we cannot find a definitive answer to the question of whether or not the Lindblad equation satisfies Condition 3 and 4 in general, with a proper choice of $\{V_n\}$. As shown in Appendix C, however, the Lindblad equation does not satisfy Condition 5, because it preserves the non-negativity of the density operator only in the positive direction in time. Given the state of a system at an instant of time t, in a deterministic theory, the state at any other instant of time (both after and before t) is uniquely determined. The Lindblad equation fails to satisfy this criterion because it does

not preserve the non-negativity of the density operator in the negative direction in time and, therefore, we cannot recover the state of the system in the past. Accordingly, we conclude that the Lindblad equation is not suitable for our purposes.

For the sake of completeness, we also investigate whether the Lindblad equation satisfies Conditions 6 to 9. In Appendix C we show that the Lindblad equation does not comply with Conditions 6 and 9. With a proper choice of $\{V_n\}$, it can be readily shown that Condition 7 is satisfied. Condition 8 is satisfied because Lindblad [1976] used it in deriving his equation. From this discussion, we conclude that the Lindblad equation is not acceptable.

Park and Band [1977, 1978a, b] searched for a generalized equation of motion linear in ρ which takes any state to a stable equilibrium state with the same values of energy, amounts of constituents and parameters as ρ. They have found that such an equation exists for two-level systems. An example is the Lindblad equation (C.4)). However, later on Simmons and Park [1981a] showed that no such linear equation exists for N-level systems with N>2, and concluded that any equation of motion which takes a state to its corresponding stable equilibrium state must be nonlinear in ρ. They have proposed Equation (5.8), which clearly satisfies their criterion, and have shown that it satisfies Conditions 1 to 4. Because once the initial density operator is given, $\hat{\rho}(\rho)$ is determined, Condition 8 is also satisfied because the equation becomes linear in ρ and its solutions are known to exist and be unique [Bender and Orszag, 1978]. However, the Park-Simmons equation satisfies Condition 7 only in an artificial manner. It is clear that the equation for a composite system takes any initial state to a stable equilibrium state of the composite system in which the individual parts are in mutual stable equilibrium with each other. However, if the equation is solved for each individual part, the resulting stable equilibrium states are not necessarily in mutual stable equilibrium. For example, the temperatures of the final states are not necessarily identical. There is no reason for them to be identical because the parts are independent of each other. The difficulty can

be avoided only by postulating that a system should first be decomposed down to its independent parts and then the Park-Simmons equation be applied to each part. Even if the problem with Condition 7 is resolved, in Appendix C we show that the equation violates Conditions 5, 6 and 9 exactly in the same manner as the Lindblad equation. Accordingly, we conclude that the Park-Simmons equation is not acceptable.

The Beretta equation (Equation (5.11)) is the most promising among the candidates given in Section 5.2. Beretta [1984] showed that his equation satisfies Conditions 1 to 6. In Appendix C, we show that the equation satisfies Condition 7 as well. The major difficulty to date has been to prove the existence and uniqueness of the solutions of the equation [Beretta, 1984], but as shown in Appendix C, this difficulty has been resolved and the Beretta equation satisfies Condition 8. In principle, the equation describes both reversible and irreversible spontaneous processes [Beretta *et al* 1984], i.e., processes in isolated systems. Because it reduces to the Schrödinger equation or, equivalently, to the von Neumann equation for mechanical states, the Beretta equation describes all the processes captured by either of these two equations. The validity of the equation for more general states ($\rho \neq \rho^2$) remains to be shown. In Chapter 6, we suggest a number of experiments which can validate quantitatively this equation and which can be used to evaluate the time constant τ. Beretta [1985a, b] also suggested an experiment for a quantitative verification of his equation of motion.

Korsch and Steffen [1987] introduced their equation in the context of subsystem dynamics. In its general form the equation results in entropy increase if initially the state is not equilibrium. Upon requiring that energy be conserved, Korsch and Steffen showed that their equation reduces to the Beretta equation, and concluded that the latter is the most general equation that satisfies all the requirements of quantum thermodynamics.

Because the Beretta equation is the only equation which complies with all the conditions stated in Section 5.1, we concur with the conclusions of Korsch and Steffen.

5.4 About the Solutions of the Beretta Equation

In this section, we discuss the solutions of the Beretta equation. We begin with a discussion of an essential feature of the solutions regarding the approach to equilibrium. Next, we present a special class of solutions which will be used frequently in Chapter 6.

5.4.1 Approach to Equilibrium

In Appendix C, we prove that the Beretta equation preserves the zero eigenvalues of the density operator. Accordingly a state having a density operator with a zero eigenvalue never reaches a stable equilibrium state, because none of the eigenvalues of the density operator of a stable equilibrium state is zero. Some authors might characterize this feature of the Beretta equation as a deficiency [Simmons and Park, 1981b]. In contrast, we believe that it is an essential and useful feature. If we require that the equation of motion takes any initial state of a system to its corresponding stable equilibrium state, the possibility that the system admits unstable (or metastable) equilibrium states is excluded. However, many experiences exist which require that they be represented by equilibrium states that are either unstable or metastable. For example, certain chemical and nuclear reactions proceed so slowly that the reactants can be conceived of as they are in equilibrium for many practical purposes. Similarly, surfaces of certain metals correspond to unstable crystallographic orientations, and for all practical purposes glasses are in equilibrium yet they are not stable. Equilibrium states that are not stable exist also in mechanics.

There is also a mathematical difficulty associated with the requirement that the equation of motion takes any state without exception to its corresponding stable equilibrium state. As we mentioned earlier, this requirement can be achieved only if the

equation of motion does not preserve the zero eigenvalues of the density operator. It turns out that an equation that does not preserve the eigenvalues would violate at least one of Conditions 5, 6, 8, or 9. The proof of this statement is given in Section C.4.

Starting with a density operator with one or more zero eigenvalue, it follows from this discussion that the approach to a stable equilibrium state can only be induced by disturbances (perturbations) that affect the dimensionality of the density operator.

5.4.2 A Special Class of Solutions of the Beretta Equation

In this section, we investigate a special class of solutions of the Beretta equation which are useful in discussions in Chapter 6, and play a role in determining how the independence of two systems is described in the equation of motion.

We consider system A associated with Hilbert space H equal to the direct product of two Hilbert spaces H_1 and H_2, i.e., $H=H_1 \otimes H_2$. We denote the identity operators on H_1 and H_2 by I_1 and I_2, respectively, and assume that the Hamiltonian operator H of A is such that

$$H = H_1 \otimes I_2 + I_1 \otimes H_2 \qquad (5.15)$$

where H_1 and H_2 are linear, closed, self-adjoint operators on H_1 and H_2, respectively. We call a Hamiltonian operator that satisfies Equation (5.15) separable. Furthermore, we assume that at time t=0, the density operator $\rho(0)$ of system A is given by

$$\rho(0) = \rho_1(0) \otimes \rho_2(0) \qquad (5.16)$$

where $\rho_1(0)$ and $\rho_2(0)$ are linear, self-adjoint, non-negative definite, unit trace operators on H_1 and H_2, respectively. We call a density operator of system A that satisfies Equation (5.16) <u>uncorrelated</u>.

In general, Equations (5.15) and (5.16) are necessary but not sufficient to establish the independence of subsystems A_1 and A_2. To see this point clearly we note the following. If the generators of motion of A_1 and A_2 are H_1 and H_2, respectively, the Beretta equation for system A is given by (see Appendix C)

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] + \frac{1}{2\tau}\{\rho, D(\rho)\}_+$$

(5.17)

where

$$D(\rho) = \frac{\begin{vmatrix} \Sigma - \langle \Sigma \rangle & \tilde{H}_1 - \langle \tilde{H}_1 \rangle & \tilde{H}_2 - \langle \tilde{H}_2 \rangle \\ (\tilde{H}_1, \Sigma) & (\tilde{H}_1, \tilde{H}_1) & (\tilde{H}_1, \tilde{H}_2) \\ (\tilde{H}_2, \Sigma) & (\tilde{H}_2, \tilde{H}_1) & (\tilde{H}_2, \tilde{H}_2) \end{vmatrix}}{\begin{vmatrix} (\tilde{H}_1, \tilde{H}_1) & (\tilde{H}_1, \tilde{H}_2) \\ (\tilde{H}_2, \tilde{H}_1) & (\tilde{H}_2, \tilde{H}_2) \end{vmatrix}}$$

(5.18)

and $\tilde{H}_1 = H_1 \otimes I_2$, and $\tilde{H}_2 = I_1 \otimes H_2$. As explained in Section C.3, this is equivalent to saying that the set of generators of motion of A is $\{\tilde{H}_1, \tilde{H}_2\}$.

On the other hand, if the only generator of motion of A is H rather than H_1 and H_2, then the Beretta equation of system A is given by Equation (5.17), but now $D(\rho)$ satisfies the relation

$$D(\rho) = \frac{\begin{vmatrix} \Sigma - \langle \Sigma \rangle & H - \langle H \rangle \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)}.$$

(5.19)

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The time evolutions resulting from the Beretta equation for the two $D(\rho)$'s (Equations (5.18) and (5.19)) are fundamentally different. If $D(\rho)$ is given by Equation (5.18), the expectation values of both H_1 and H_2 are conserved and subsystems A_1 and A_2 evolve only along states that preserve both energies. Of course, the energy $<H>$ of A is also conserved because $<H>=<H_1>+<H_2>$. On the other hand, if $D(\rho)$ is given by Equation (5.19), the energy $<H>$ is conserved but, in general $<H_1>$ and $<H_2>$ are not. Here the state space of system A is broader than when both $<H_1>$ and $<H_2>$ are conserved, and subsystems A_1 and A_2 can no longer be considered independent.

The last observation brings forth an important distinction between quantum mechanics and quantum thermodynamics. In the former theory, if the Hamiltonian operator is separable and the initial density operator is uncorrelated, it is easy to show that the solution $\rho(t)$ of the von Neumann equation satisfies at all times the relation

$$\rho(t) = \rho_1(t) \otimes \rho_2(t) \tag{5.20}$$

where $\rho_1(t)$ and $\rho_2(t)$ is the solution of the von Neumann equation corresponding to the relevant subsystem, i.e.,

$$\frac{\partial \rho_i}{\partial t} = \frac{1}{i\hbar}\left[H_i, \rho_i\right] \quad i = 1, 2. \tag{5.21}$$

Therefore, we conclude that the subsystems A_1 and A_2 are independent of each other, hence they are subsystems of the composite system A. In other words, the separability of the Hamiltonian, combined with an initial uncorrelated density operator, is sufficient to establish the permanent independence of the two subsystems. In quantum thermodynamics, the situation is different. If $\rho(0)$ and $D(\rho)$ are given by Equations (5.16) and (5.19), the density operator at any instant of time t is still given by Equation (5.20), but each of $\rho_1(t)$ and $\rho_2(t)$ is not a solution of the equation relevant to the subsystem, i.e.,

$$\frac{\partial \rho_i}{\partial t} \neq \frac{1}{i\hbar}[H_i, \rho_i] + \frac{1}{2\tau}\left\{\rho_i, \frac{\begin{vmatrix} \Sigma_i - \langle\Sigma_i\rangle & H_i - \langle H_i\rangle \\ (H_i, \Sigma_i) & (H_i, H_i) \end{vmatrix}}{(H_i, H_i)}\right\}_+ \quad i = 1,2.$$ (5.22)

The reason is that, in general neither $\langle H_1 \rangle$ nor $\langle H_2 \rangle$ is conserved. Therefore, the separability of the Hamiltonian, combined with an initial uncorrelated density operator, is not sufficient to describe independence of the two subsystems.

At this point, we can introduce the notion of the temperature of a subsystem which is necessary for discussions presented in the remaining portion of this chapter, and Chapter 6. We consider a composite system A of two subsystems A_1 and A_2, and an uncorrelated density operator $\rho = \rho_1 \otimes \rho_2$ of system A, such that each of ρ_1 and ρ_2 corresponds to a canonical distribution (Equation (4.8))

$$\rho_i = \frac{\exp(-\beta_i H_i)}{\text{Tr}(\exp(-\beta_i H_i))}, \quad \beta_i = \frac{1}{kT_i} \quad i = 1,2$$ (5.23)

Then we call T_1 and T_2 the temperatures of subsystem A_1 and A_2, respectively, regardless of the independence of the subsystems.

There are well-known examples of systems whose time evolutions are given by Equations (5.17) and (5.19). The first is a structureless particle in a force-free rectangular box. The Hamiltonian can be separated into three parts, one along each of the x, y, and z direction. Therefore, we can conceive of system A as a composite of three subsystems A_x, A_y, and A_z. In innumerable experiments, it has been shown that if initially the temperatures of subsystems A_x, A_y, and A_z are different, the system exhibits a relaxation and eventually reaches a stable equilibrium state where the temperatures of the

subsystems are identical. Therefore, the time evolution of each subsystem is influenced by the other two subsystems, i.e., the subsystems are not independent.

Another example is a diatomic gas molecule in a force-free rectangular container. The Hamiltonian operator of the system is separable into two parts H_{tr} and H_{vib}, associated with the translational and vibrational degrees of freedom of the molecule, respectively. It is experimentally observed that any initial difference in the temperatures of subsystems A_{tr} and A_{vib} vanishes as the system evolves. This phenomenon is called vibrational relaxation in a diatomic gas [Lambert, 1977]. Again, the two subsystems influence each other's time evolution hence they are not independent.

One last example is an elementary particle with non-zero spin. The Hamiltonian of this one particle system can be divided into two parts H_{tr} and H_s, associated with the translational and spin degrees of freedom of the particle, respectively. Again, it is experimentally observed that the system exhibits a relaxation, i.e., any difference in the initial temperatures of subsystems A_{tr} and A_s decays during the time evolution of the system. This phenomenon is an example of spin relaxation observed in innumerable experiments [Guyer *et al*, 1971].

Now we study the special class of solutions mentioned at the beginning of the section. We consider a system A that is composite of two subsystems A_1 and A_2 which are not subsystems of A. For the sake of simplicity, we assume that the only generator of the motion of system A is the Hamiltonian operator H, and that initially subsystems A_1 and A_2 have different temperatures T_1 and T_2, respectively (Equation (5.23)). In Appendix C, we show that the solution $\rho(t)$ of the Beretta equation is uncorrelated at any instant of time t, i.e., it is given by

$$\rho(t) = \rho_1(t) \otimes \rho_2(t) \tag{5.24}$$

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where $\rho_1(t)$ and $\rho_2(t)$ correspond to canonical distributions (Equation (5.23)) with time dependent temperatures $T_1(t)$ and $T_2(t)$, respectively. Furthermore, the inverse temperatures satisfy the relation

$$\frac{d(\beta_1 - \beta_2)}{dt} = -\frac{1}{\tau}(\beta_1 - \beta_2), \quad \beta_i = \frac{1}{kT_i} \quad i = 1,2 \tag{5.25}$$

where τ is the time constant in the Beretta equation. This result can readily be generalized to systems with many generators of motion, and to systems which admit more than two subsystems. This class of solutions plays an important role in the description of relaxation phenomena, and to the best of our knowledge is identified for the first time.

Chapter 6

6. Experimental Verification

The purpose of this chapter is to provide experimental evidence of the validity of quantum thermodynamics. To achieve our goal, in Section 6.1 we present two spin relaxation experiments reported in the literature. The results of both experiments are in qualitative agreement with the predictions of the Beretta equation. The first experiment provides also a preliminary estimate for the time constant τ in the Beretta equation. The second experiment needs to be perfected to establish a quantitative comparison with the predictions of the Beretta equation. Therefore, in Section 6.1.4 we suggest a new experiment which is a combination of the two experiments we discuss, and which can be used to validate the Beretta equation to a great degree of accuracy. We believe that the suggested experiment is feasible because it relies on the technologies used in the other two experiments. In Section 6.2 we show that under suitable conditions the Beretta equation reduces to phenomenological equations of irreversible thermodynamics whose validity is shown in innumerable experiments.

6.1 Two Spin Relaxation Experiments

In this section we present two spin relaxation experiments which are consistent with the premises of quantum thermodynamics. In both experiments, the time evolution of the spin of the valence electron of Rubidium (Rb) is studied by means of the technique called "optical pumping". Before presenting the results of the two experiments, we review the method of "optical pumping".

6.1.1 Optical Pumping

A detailed description of optical pumping is given by Bernheim [1965]. We consider an alkali metal atom (e.g., Na, Rb) which has a $^2S_{1/2}$ ground state, and $^2P_{1/2}$ first excited state, as shown in Figure 6.1. The radiative transition from the first excited state to the ground state results in the emission of a photon with energy $h\nu_1$.
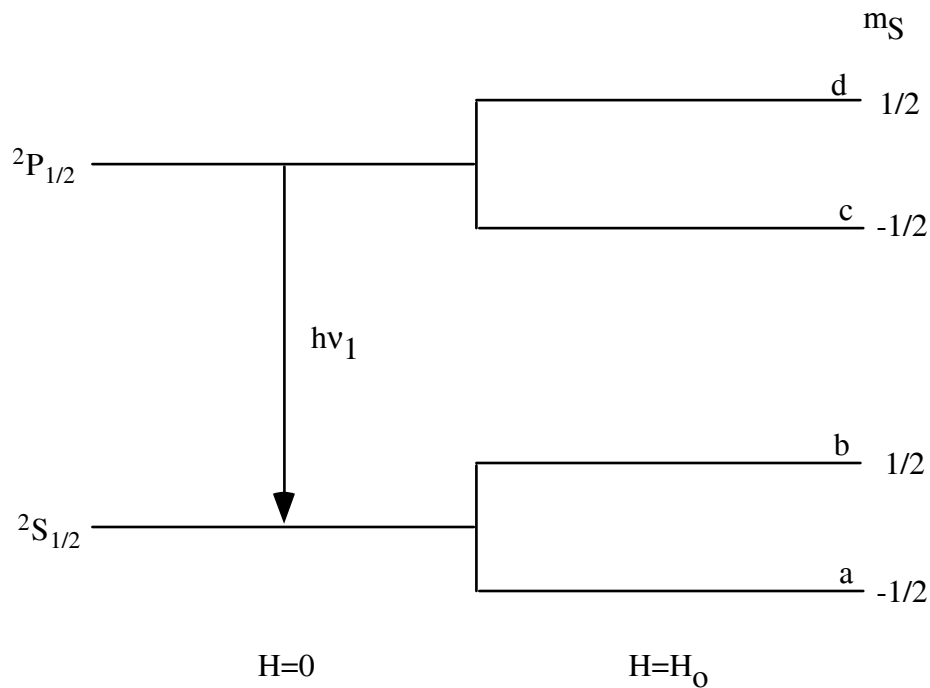

Figure 6.1 Energy levels of hypothetical alkali metal atom

If an alkali metal atom is placed in a magnetic field H_0, the splittings in the energy levels are as shown in Figure 6.1. We denote the magnetic quantum number of the atomic state by m_s. A typical experimental setup is shown in Figure 6.2. A spectral lamp of the alkali metal studied is used in the pumping. The component of the pumping light consisting of photons with energy $h\nu_1$ is called the D_1 resonance radiation. The light emitted by the lamp is focused with lenses, and then passes through an interference filter where the component of the pumping light corresponding to photon energies other

than $h\nu_1$ is attenuated. After the interference filter, the pumping light passes through a circular polarizer.. The circularly polarized D_1 resonance radiation then passes through a vapor cell which contains the vapor of the alkali metal species. The vapor cell is placed in a weak magnetic field, H_0, which is directed along the direction of the light path. In a typical optical pumping experiment, the intensity of the D_1 resonance radiation passing through the apparatus is also measured with a photo tube.

Figure 6.2 Schematic of an optical pumping apparatus

The effect of the circularly polarized D_1 radiation upon the atoms in the vapor cell can be summarized as follows. The atoms will be excited to the $^2P_{1/2}$ state with a selection rule of $\Delta m_s = \pm 1$. Furthermore, the selection rule will be either $\Delta m_s = +1$ or $\Delta m_s = -1$ but not both. Which one holds depend upon the direction of the magnetic field with respect to the direction of propagation of light and the direction of polarization. We consider the case where the condition $\Delta m_s = +1$ is satisfied.

Inspection of Figure 6.1 reveals that there is only one possible excitation that can take place. Excitation with $\Delta m_s = +1$ can occur only from energy level a to energy level d. The lifetimes of the $^2P_{1/2}$ states of alkali metal atoms are typically of the order of 10^{-8} seconds. If we assume that no disorientation occurs in the excited state of the atom (i.e.,

the state c is not populated) the atom will fluoresce from state d to states a and b with equal transition probability. For an assembly of atoms the net effect in time will be a transfer of population from state a to state b. This effect is called <u>optical pumping</u>.

We consider a single alkali metal atom. The Hamiltonian of the system is separable into two parts H_s and H_{tr}, corresponding to the atomic levels of the valence electron and the translational degrees of freedom, respectively. We consider that the nucleus and the electrons other than the valence electron are tightly bound together, and therefore are treated as a single structureless point mass. We define the two subsystems A_s and A_{tr} associated with each part of the Hamiltonian H_s and H_{tr}, respectively.

Before the pumping radiation is turned on, the atom is in a stable equilibrium state, and the density operator ρ_s associated with the atomic levels of the valence electron corresponds to the canonical distribution which here is

$$\rho_s = \frac{\exp\left(-\frac{1}{kT}H_s\right)}{\mathrm{Tr}\left(\exp\left(-\frac{1}{kT}H_s\right)\right)} \tag{6.1}$$

We denote the energy eigenvalues corresponding the levels a,b,c,… by $\varepsilon_a, \varepsilon_b, \varepsilon_c,…$ Accordingly, we denote the diagonal elements of ρ_s by $p_a, p_b, p_c,…$, i.e., p_a represents the probability of getting energy measurement result ε_a, when the system is in the state $\{\varepsilon, \rho_s \otimes \rho_{tr}\}$.

In a typical optical pumping experiment, the temperature of the alkali metal vapor is kept between 30^oC and 70^oC and the strength of the magnetic field used is less than 0.02G. Thus difference between p_a and p_b is about 1 part in a million, and p_c and the probabilities associated with higher energy levels are extremely small ($<10^{-26}$). Therefore, we can effectively describe the subsystem A_s as a two-level system, i.e., we can use a two-dimensional Hilbert space H_s in representing A_s. We call A_s, the spin

subsystem because it is characterized by the spin of the valence electron. In this simplified representation, the density operator ρ_s (Equation (6.1)) of the spin subsystem before turning on the pumping light, in the energy representation is given by

$$\rho_s = \frac{1}{\exp(-\beta\varepsilon_a)+\exp(-\beta\varepsilon_b)}\begin{bmatrix} \exp(-\beta\varepsilon_b) & 0 \\ 0 & \exp(-\beta\varepsilon_a) \end{bmatrix} = \begin{bmatrix} p_b & 0 \\ 0 & p_a \end{bmatrix} \tag{6.2}$$

where $\beta=1/kT$, T is the temperature, and $p_a \approx p_b \approx 1/2$. Accordingly, the spin Hamiltonian H_s in the energy representation is given by

$$H_s = \begin{bmatrix} \varepsilon_b & 0 \\ 0 & \varepsilon_a \end{bmatrix}. \tag{6.3}$$

where ε_a and ε_b are the energies of levels a and b, respectively.

The probability that an atom absorbs the pumping light is proportional to the lower diagonal element of ρ_s in energy representation, i.e., to p_a in Equation (6.2). In typical optical pumping experiments the intensity of the pumping light passing through the vapor cell (denoted by I_1 in Figure 6.2) is monitored by means of a photo tube, which allows the observer to determine instantaneous values of p_a and p_b.

Before going into the discussion of the experiments, we would like to reiterate an important distinction between the non-statistical approach adopted in this dissertation and the statistical approach found in the literature. We will emphasize this distinction before the pumping light is turned on. In quantum thermodynamics each alkali metal atom is characterized by the same density operator, i.e. ,

$$\rho(0) = \rho_{tr} \otimes \rho_s = \frac{\exp(-\beta H_{tr})}{\text{Tr}(\exp(-\beta H_{tr}))} \otimes \frac{\exp(-\beta H_s)}{\text{Tr}(\exp(-\beta H_s))}. \tag{6.4}$$

In statistical quantum mechanics on the other hand, a fraction p_a of the atoms is in level a and a fraction p_b in level b.

6.1.2 Franzen Experiment

The experiment by Franzen [1959] is intended to evaluate the spin relaxation time constant of Rb vapor under different conditions. By using the optical pumping technique, p_b is increased to almost unity. By means of a mechanical shutter, the pumping light is cut off. It is then observed that p_b starts decreasing and eventually reaches its equilibrium value of 1/2 (i.e., $p_a=p_b$). The measurement of p_a is performed by reopening the shutter and allowing the pumping light pass through the vapor cell. The intensity of the light passing through the tube gives a direct measure of p_a and, therefore, p_b because $p_a+p_b=1$. The decay in p_b is shown to be close to exponential. The decay constants are evaluated under different experimental conditions.

In statistical quantum mechanics, no relaxation is predicted, because the von Neumann equation preserves the diagonal entries of the density operator in the energy representation. In the literature, this difficulty is avoided by attributing the relaxation to collisions between Rb atoms, and between Rb atoms and the walls of the vapor cell. To reduce the collision frequency of a single Rb atom with other Rb atoms and the walls, different buffer gases are employed, such as Ne, Ar, Kr, and Xe. These gases, however, introduce collisions between their molecules and Rb atoms, collisions that contribute to the spin relaxation.

Franzen studied the effect of different buffer gases on spin relaxation. However, his most important results are obtained in an evacuated cell in which case there was no buffer gas. Without use of buffer gas, it is very difficult to achieve optical pumping because the interactions between the Rb atoms and the cell walls result in very short relaxation times. Franzen, however, uses a special technique which avoids this difficulty.

He lines the vapor cell with a thin film of tetracontane ($C_{40}H_{82}$). This coating material allows the experiment to be done in an evacuated cell, and achieves a relaxation time of the order of 80-90 ms. The relaxation times reported for different Rb vapor pressures are shown in Figure 6.3.

The tetracontane lining performed well, and Franzen concluded that the only contribution to spin relaxation in an evacuated cell comes from the collisions between Rb atoms. The number of collisions made by a single Rb per unit time, called the collision frequency, is proportional to the vapor pressure in the range of interest of the experiment. Therefore, if collisions between Rb atoms are the main contributors to the relaxation, the relaxation time should be inversely proportional with the Rb vapor pressure. This description, however, is not in agreement with the experimental results shown in Figure 6.3. At relatively high vapor pressures, the relaxation time exhibits the behavior predicted by the collision description. At vapor pressures below 2×10^{-6} mm Hg, however, the relaxation time constant is independent of the vapor pressure.
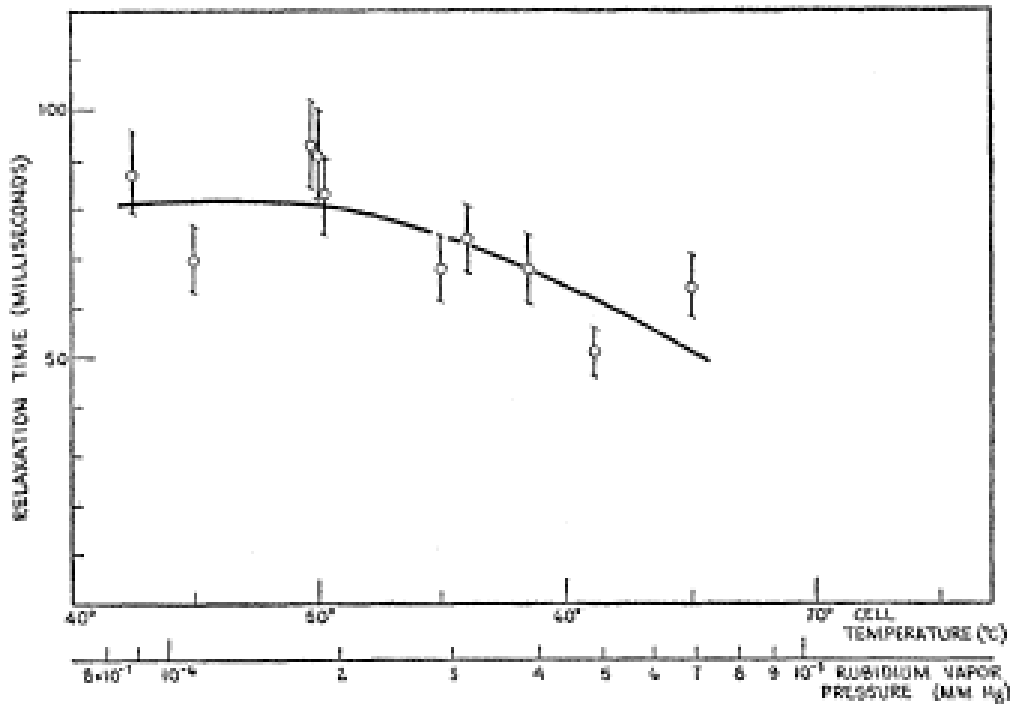

Figure 6.3 Variation of relaxation time with rubidium vapor pressure

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The constant values of the relaxation times at low pressures are consistent with quantum thermodynamics and the Beretta equation. The convergence of the relaxation time to a constant value as the vapor pressure decreases suggests an internal relaxation mechanism in the one atom system and this is inherent in the Beretta equation.

Because the heat capacity of the translational degrees of freedom (subsystem A_{tr}) is much larger than that of the spin (subsystem A_s), we can effectively assume that A_{tr} acts like a reservoir. Before the pumping is turned on, the density operator of the one atom system is given by Equation (6.4), and accordingly the density operator of the spin subsystem by Equation (6.2). As a result of optical pumping, the system reaches a steady state in which the density operator of the spin subsystem in the energy representation is given by

$$\rho_s(0) = \begin{bmatrix} 1-\delta & 0 \\ 0 & \delta \end{bmatrix} \tag{6.5}$$

where $0 < \delta << 1$. The term δ is not zero because the optical pumping process competes continuously with the radiative decay of excited levels. The density operator of the translational subsystem is not affected by the optical pumping process, and remains in the form of a canonical distribution corresponding to cell temperature T_{tr}. A time t=0, we turn off the pumping light. Noting that the density operator given by Equation (6.5) can be conceived of as a canonical distribution with a negative spin temperature T_s, the time development of the density operator according to the Beretta equation is given by Equations (5.24) and (5.25)

$$\rho(t) = \rho_s(t) \otimes \rho_{tr}(t) \tag{6.6}$$

$$\frac{d(\beta_s - \beta_{tr})}{dt} = -\frac{1}{\tau}(\beta_s - \beta_{tr}), \quad \beta_i = \frac{1}{kT_i} \quad i = s, tr \tag{6.7}$$

where $\rho_s(t)$ and $\rho_{tr}(t)$ are canonical distributions with time dependent temperatures $T_s(t)$ and $T_{tr}(t)$, respectively. It can be easily shown that the inverse spin temperature decays exponentially and that the decay constant is the time constant τ given in the Beretta equation. Therefore the Franzen experiment provides a preliminary estimate of 80-90 ms for the time constant τ.

As we have mentioned before, in both statistical quantum mechanics and quantum thermodynamics, if the density operator is given by the canonical distribution there is no motion in the ordinary space (expectation value of linear momentum is zero). Therefore, the dependence of the time constant on the collision frequency calculated classically needs to be explained. At relatively low vapor pressures, each Rb atom can be regarded as a system, and its internal relaxation can be studied independent of the other Rb atoms. At relatively high Rb vapor pressure ($>2 \times 10^{-6}$ mm Hg), each single atom cannot be considered as a system because of the inter-atomic interactions. Here we need to use the many particle Hamiltonian operator to describe the behavior of the vapor. With such an operator, it is difficult to obtain explicit numerical results for direct comparison with experiments.

6.1.3 Kukolich Experiment

Another spin-relaxation experiment was performed by Kukolich [1967], and suggested by Prof. R. Weiss as a demonstration of the Schrödinger equation in a course on quantum mechanics given at MIT. The experimental setup is quite similar to that of Franzen. Optical pumping is used to achieve a nonequilibrium spin state of Rb atoms. The buffer gas is Ne. As in the case of Franzen experiment p_b is increased to almost unity. Rather than cutting off the pumping light by means of a shutter and observing the relaxation of spin along the z direction, Kukolich quickly switched the magnetic field

from the z to the x direction. The light transmitted through the rubidium vapor is used as a probe to measure the occupation values of levels A and B.

Because the Kukolich experiment is suggested to show the validity of the von Neumann or, equivalently, the Schrödinger equation, first we present the predictions of statistical quantum mechanics. Initially the magnetic field is in the z direction, and the Hamiltonian operator in the energy representation is given by

$$H_z = \begin{bmatrix} \varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix} \qquad (6.8)$$

After a long pumping period, the initial density operator of the spin subsystem in the H_z representation is given by Equation (6.5)

$$\rho_s(0) = \begin{bmatrix} 1-\delta & 0 \\ 0 & \delta \end{bmatrix} \qquad (6.9)$$

where $0<\delta<<1$. At t=0, we assume that the magnetic field is switched from the z to the x direction. Thus the Hamiltonian H_s in the H_z representation is given by

$$H_s = \begin{bmatrix} 0 & \varepsilon \\ \varepsilon & 0 \end{bmatrix}. \qquad (6.10)$$

The solution of the von Neumann equation can be calculated, and is given in the H_z representation by

$$\rho(t) = \begin{bmatrix} (1-\delta)\cos^2\omega t + \delta\sin^2\omega t & i(1-2\delta)\cos\omega t\,\sin\omega t \\ -i(1-2\delta)\cos\omega t\,\sin\omega t & (1-\delta)\sin^2\omega t + \delta\cos^2\omega t \end{bmatrix}, \qquad (6.11)$$

where $\omega = \varepsilon / \hbar$. Using well-known trigonometric relations, it is easy to verify that this solution is periodic of period π/ω. Hence, according to statistical quantum mechanics, it is expected that the solution and hence the diagonal elements of ρ in the H_z representation oscillate in time with a frequency of ω/π.

The results of the experiment are shown in Figure 6.4. The author concluded that the experiment validates the Schrödinger equation because of the observed oscillation in the intensity of the light passing through the vapor cell. However, the Schrödinger equation implies no decay of oscillations whereas the experimental results do decay. The author attributed this decay to the inhomogeneities in the magnetic field but did not provide any quantitative analysis.
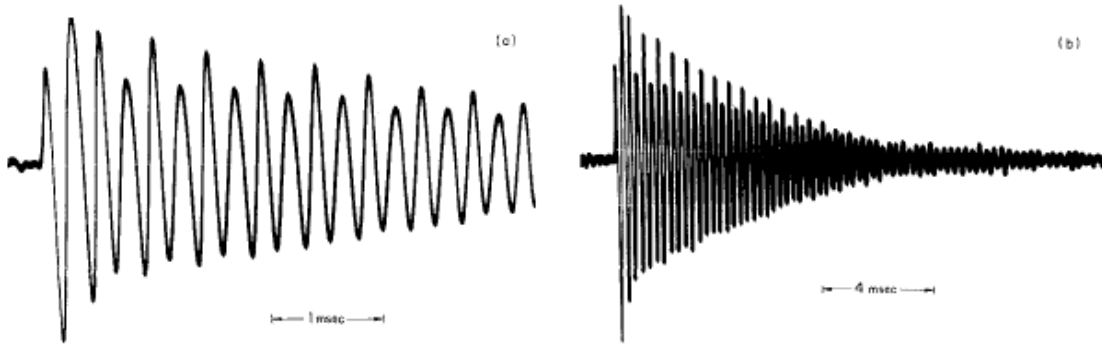

Figure 6.4 Experimental photo tube current as a function of time after the field
is switched to the x direction

The decay in the intensity of the oscillation of the pumping light passing through the vapor cell is predicted, however, in quantum thermodynamics. To show this point, we express the density operator at time t=0 (Equation (6.9)) in the H_s representation, so that

$$\rho_s(0) = \begin{bmatrix} 1/2 & 1/2 - \delta \\ 1/2 - \delta & 1/2 \end{bmatrix}. \tag{6.12}$$

In the same representation, the Hamiltonian H_S is given by

$$H_s = \begin{bmatrix} \varepsilon & 0 \\ 0 & -\varepsilon \end{bmatrix}. \tag{6.13}$$

From Equations (6.12) and (6.13), we conclude that at t=0 <H>=0. The Beretta equation takes the initial nonequilibrium state to the corresponding stable equilibrium state. Because the translational subsystem behaves like a reservoir, the temperature of the stable equilibrium state will be the initial temperature of the vapor cell ($\approx 30^o$C). At this temperature $\varepsilon/kT \approx 0$, and the density operator of the spin subsystem in the H_s representation is given by

$$\rho_s(\infty) = \begin{bmatrix} 1/2 & 0 \\ 0 & 1/2 \end{bmatrix}. \tag{6.14}$$

Therefore, at this state p_a is 1/2, i.e., the amplitude of the oscillation of the intensity of the pumping light decays, which is in agreement with the result of the Kukolich experiment shown in Figure 6.4.

Even though no closed analytic expression is available for the solution of the Beretta equation to date, an approximate solution can be provided in the case of the Kukolich experiment. First, we assume that the temperature of the vapor cell is very large which is equivalent to saying that $\varepsilon/kT=0$. Then it is straightforward to show that the time evolution of the density operator is given by

$$\frac{\partial \rho_s}{\partial t} = \frac{1}{i\hbar}[H_s, \rho_s] + \frac{1}{2\tau}\left\{\rho_s, \frac{\begin{vmatrix} \Sigma_s - \langle \Sigma_s \rangle & H_s - \langle H_s \rangle \\ (H_s, \Sigma_s) & (H_s, H_s) \end{vmatrix}}{(H_s, H_s)}\right\}_+ \tag{6.15}$$

which is the Beretta equation for a two-level system. Beretta [1985a] provided a solution to this equation, and showed that the amplitude of the oscillations r(t) of the diagonal elements of ρ_S in the H_z representation is given by

$$r(t) = \tanh\left(\frac{1}{2}\exp(-t/\tau)\text{Log}\left(\frac{1+r(0)}{1-r(0)}\right)\right). \tag{6.16}$$

The amplitude r(t) is also the amplitude of the oscillations in the intensity of the pumping light passing through the vapor cell. Equation (6.16) predicts a non-exponential decay in these oscillations. Because the reported experimental results do not include numerical data, we are unable to determine whether the decay phenomenon shown in Figure 6.4 is exponential or not. Nevertheless, qualitatively the Beretta equation agrees with the results shown in Figure 6.4. Therefore, we conclude that the Kukolich experiment provides an additional indication for the validity of the Beretta equation rather than the von Neumann equation. It is noteworthy that, in general, because the spin subsystem is not independent of the translational subsystem, its time evolution is not described by the Beretta equation for a two-level system. However, in the experiment we just decribed, the spin subsystem obeys the Beretta equation for a two-level system, because the temperature and the heat capacity of the translational subsystem are very large.

Kukolich attributed the decay in the diagonal elements of ρ_S in the H_z representation to the inhomogeneities in the magnetic field, but he did not give any quantitative results. In the case of Franzen, however, the inhomogeneities in the magnetic field are not included in the discussion, and yet he was able to describe the relaxation consistently. To resolve the question of whether the field inhomogeneities are responsible for the relaxation, studies with inhomogeneous magnetic fields can also be performed.

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6.1.4 A Suggested Experiment

Combining the results of Kukolich and Franzen, we suggest the Franzen experiment be repeated with a slightly different setup. The use of Ne buffer gas eliminates the use of the single atom approximation. Therefore, we suggest that the experiment is performed in an evacuated cell lined with tetracontane as in the case of Franzen The vapor pressure must be chosen lower than 2×10^{-6} mm Hg so that the contribution of interatomic interactions to the relaxation process becomes negligible, in other words the single atom model becomes more accurate. Furthermore, there is a possibility of repeating the experiment with different initial conditions. This would allow a better comparison of the predictions of the Beretta equation with the experimental results. To achieve different initial conditions a shutter similar to that of Franzen can be employed. We can turn off the pumping light at time t=0, and then switch the magnetic field from the z direction to the x direction at time t'>0. Evaluating the spin-relaxation time using Franzen's method, it is possible to determine the density operator of the spin subsystem at the time t'.

Finally, instead of using a single pumping light in the z direction, three perpendicular pumping lights can be used simultaneously. This information is equivalent to knowing the value of all three components of the spin angular momentum, which in turn uniquely determines the density operator of the spin subsystem. Therefore, the evolution of the density operator (and not only the time evolution of the diagonal elements of it in the H_z representation) can be experimentally evaluated.

It is noteworthy that, even if the Beretta equation is not the correct equation of motion, the experiments just cited still show the validity of quantum thermodynamics. The reason is that, in general, quantum thermodynamics implies an internal relaxation of a single atom system, and therefore agrees qualitatively with the experiments. On the other hand, statistical quantum mechanics does not imply such a relaxation if the equation

of motion is the von Neumann equation and, therefore, does not agree even qualitatively with the experiments. In the literature, there are attempts in describing the relaxation phenomenon within the framework of statistical quantum mechanics by using the so-called master equations. However, as noted by Wolf [1979], the master equations are not derived from the von Neumann equation and their validity is postulated. But this approach is inconsistent with the statistical aspect of the theory, for the unique generalization of the Schrödinger equation in the statistical theory results in the von Neumann equation and not in the master equations.

 On the contrary, statistical quantum mechanics does not imply such a relaxation and, therefore, does not agree even qualitatively with the experiments.

As a final remark, we would like to emphasize that, following the current practice in the literature, we have treated the ground state of the Rb atom as having spin 1/2. Due to its coupling to the nuclear spin, however, the spin of the ground state is 2. Though the formulation needs to be modified, the modification would have no effect on the general aspects of the solution of the Beretta equation, because the spin relaxation is predicted independent of the value of spin. Even though a closed form solution of the Beretta equation is not available for a spin 2 system, a numerical approximation to any desired degree of accuracy can always be obtained and compared to experimental results.

6.2 Onsager Reciprocal Relations

Many phenomenological equations have been proposed in the literature. They correlate with great success many practical phenomena. Sometimes, they are referred to as phenomenological equations of irreversible thermodynamics. The general form of these equations are [Beretta, 1987]

$$\frac{d}{dt}\begin{bmatrix} \langle X_1 \rangle \\ \cdots \\ \langle X_n \rangle \end{bmatrix} = \begin{bmatrix} L_{11} & \cdots & L_{1n} \\ \cdots & \cdots & \cdots \\ L_{n1} & \cdots & L_{nn} \end{bmatrix}\begin{bmatrix} f_1 \\ \cdots \\ f_n \end{bmatrix} \qquad (6.17)$$

where $\{X_i\}$ is a set of n operators corresponding to observables associated with the system, $\left\{\dfrac{d\langle X_i \rangle}{dt}\right\}$ is the set of "dissipative fluxes" associated with these observables, and $\{f_i\}$ is the associated set of forces. Each coefficient L_{mn} is called a "dissipative conductivity".

For a two-dimensional heat conduction in an anisotropic medium, Onsager [1931] postulated that the square matrix in Equation (6.17) satisfies the reciprocity relations

$$L_{ij} = L_{ji} \quad \forall i, j. \qquad (6.18)$$

Later, Casimir [1945] showed that the reciprocity relations are valid for a large class of processes. In this section, we show that the phenomenological equations of irreversible thermodynamics can be obtained from the Beretta equation. In contrast, it is noteworthy that the phenomenological equations cannot be derived from the Schrödinger or the von Neumann equation, because each of the last two equations describes only reversible phenomena.

Beretta [1987] studied the relations between fluxes and forces in a general manner. His work is limited to systems associated with finite dimensional Hilbert spaces, however. For a class of states, in this section we show that the proof of Beretta remains valid even for a system with an infinite dimensional Hilbert space, and that the forces can be expressed as a differences in the temperatures and in the chemical potentials of two subsystems.

First, we present the result obtained by Beretta. He considered a density operator given by

$$\rho = \frac{B \, \exp\left(-\sum_i f_i X_i\right)}{Tr\left(B \, \exp\left(-\sum_i f_i X_i\right)\right)} \tag{6.19}$$

where B is a projection operator obtained from ρ by substituting each of the nonzero eigenvalues with unity, $\{f_i\}$ is a set of real scalars, and $\{X_i\}$ is a set of linear operators corresponding to observables. For such an operator, Beretta showed that his equation results in the Equation (6.17), and the Onsager reciprocal relations given by Equation (6.18).

In Beretta's proof, however, the cardinality of the set $\{X_i\}$ is chosen large enough that any density operator can be expressed as in Equation (6.19). If the dimensionality of the Hilbert space associated with the system is infinite, the set $\{X_i\}$ should contain infinitely (countably) many operators, and Equation (6.17) involves an infinite by infinite matrix. To avoid this difficulty Beretta restricted his result to a finite dimensional Hilbert space. After all, the power of the phenomenological equations lies in their simplicity, and the dimension of the matrix given in Equation (6.17) is always finite.

For a certain class of states and a set $\{X_i\}$ smaller than the one considered by Beretta, we obtain Beretta's result. For the sake of simplicity, we consider a system A whose only generators of motion are the Hamiltonian operator H and the number operator N of the single constituent. We assume that system A admits two subsystems A_1 and A_2 associated with the Hamiltonian operators H_1 and H_2, and the number of constituents operators N_1 and N_2, respectively, i.e., $H=H_1+H_2$, and $N=N_1+N_2$. Furthermore, at time $t=0$, the density operator satisfies the relation

$$\rho(0) = \rho_1(0) \otimes \rho_2(0). \tag{6.20}$$

where the density operators of the two subsystems are given by the grand canonical distributions

$$\rho_i(0) = \frac{\exp(-\beta_i H_i - \nu_i N_i)}{\mathrm{Tr}(\exp(-\beta_i H_i - \nu_i N_i))} \quad \beta_i = \frac{1}{kT_i}, \quad \nu_i = -\frac{\mu_i}{kT_i} \quad i = 1, 2 \tag{6.21}$$

where T_1 and T_2 are the temperatures, and μ_1 and μ_2 are the chemical potentials of subsystems A_1 and A_2, respectively. We show in Appendix C that the density operator of the system satisfies the relation

$$\rho(t) = \rho_1(t) \otimes \rho_2(t) \quad \forall t \geq 0 \tag{6.22}$$

where $\rho_1(t)$ and $\rho_2(t)$ are given by grand canonical distributions with time dependent temperatures and chemical potentials. In other words, the density operator of system A is given by Equation (6.17) at any instant of time, and the set $\{X_i\}$ contains only four operators H_1, H_2, N_1, and N_2 regardless of the dimensionality of the Hilbert space associated with system A. Therefore, the result of Beretta applies directly, i.e., we obtain the set of equations

$$\frac{d}{dt}\begin{bmatrix} \langle H_1 \rangle \\ \langle H_2 \rangle \\ \langle N_1 \rangle \\ \langle N_2 \rangle \end{bmatrix} = \begin{bmatrix} L_{11} & L_{12} & L_{13} & L_{14} \\ L_{21} & L_{22} & L_{23} & L_{24} \\ L_{31} & L_{32} & L_{33} & L_{34} \\ L_{41} & L_{42} & L_{43} & L_{44} \end{bmatrix} \begin{bmatrix} \beta_1 \\ \beta_2 \\ \nu_1 \\ \nu_2 \end{bmatrix} \tag{6.23}$$

with $L_{ij} = L_{ji}$ for all i and j. This is not exactly the form of phenomenological equations found in the literature, however, where the forces are expressed as a difference in the

inverse temperature of the subsystems, i.e., β_1-β_2, or as a difference in the chemical potentials of the subsystems, i.e., ν_1-ν_2.

To obtain the required form, we note that $\dfrac{d\langle H\rangle}{dt}=\dfrac{d\langle H_1\rangle}{dt}+\dfrac{d\langle H_2\rangle}{dt}=0$ and $\dfrac{d\langle N\rangle}{dt}=\dfrac{d\langle N_1\rangle}{dt}+\dfrac{d\langle N_2\rangle}{dt}=0$, for all states. Therefore, in addition to satisfying the reciprocity relations, the matrix in Equation (6.23) has the following property: the sum of the first and second rows, and the sum of the third and fourth rows must vanish. Using this information, it is straightforward to show that Equation (6.23) reduces to

$$\frac{d}{dt}\begin{bmatrix}\langle H_1\rangle\\ \langle H_2\rangle\\ \langle N_1\rangle\\ \langle N_2\rangle\end{bmatrix}=\begin{bmatrix}L_{11} & -L_{11} & L_{13} & -L_{13}\\ -L_{11} & L_{11} & -L_{13} & L_{13}\\ L_{13} & -L_{13} & L_{33} & -L_{33}\\ -L_{13} & L_{13} & -L_{33} & L_{33}\end{bmatrix}\begin{bmatrix}\beta_1\\ \beta_2\\ \nu_1\\ \nu_2\end{bmatrix}. \tag{6.24}$$

This equation can be rewritten in a more convenient form given by

$$\frac{d}{dt}\begin{bmatrix}\langle H_1\rangle-\langle H_2\rangle\\ \langle N_1\rangle-\langle N_2\rangle\end{bmatrix}=\begin{bmatrix}2L_{11} & 2L_{13}\\ 2L_{13} & 2L_{33}\end{bmatrix}\begin{bmatrix}\beta_1-\beta_2\\ \nu_1-\nu_2\end{bmatrix} \tag{6.25}$$

where $\dfrac{d}{dt}$ (<H$_1$>-<H$_2$>) is the energy flux between subsystems 1 and 2, $\dfrac{d}{dt}$ (<N$_1$>-<N$_2$>) is the constituent flux between subsystems 1 and 2, and the driving forces are expressed in terms of the differences in the temperatures and chemical potentials. To the best of our knowledge, this derivation is done for the first time.

Even though our discussion is restricted to systems that admit only two subsystems, the generalization of the result obtained to more complicated systems is straightforward. So, we have shown that, under suitable conditions, the Beretta equation reduces to the phenomenological equations of irreversible thermodynamics.

Chapter 7

7. Two Open Problems

In this chapter, we present our reflections on two unresolved problems. In Section 7.1, we address a problem related to the value of entropy assigned to stable equilibrium states with zero temperature. In Section 7.2, we investigate an intriguing problem related to triple points of pure substances.

7.1 The Value of Entropy at Zero Temperature

In this section, we investigate the lowest value of entropy attained by the stable equilibrium states of a system. The concavity of the stable-equilibrium-states curve implies that this minimum is attained when the temperature is also a minimum. In quantum thermodynamics, the lowest value of temperature attained is zero, therefore, the stable equilibrium state having zero temperature admits the smallest value of entropy among all the stable equilibrium states of the system.

First, we consider a petit system, i.e., a system that does not admit fractional expectation values of amounts of constituents. The density operator corresponding to a stable equilibrium state of a petit system is given by the canonical distribution (Equation (4.8))

$$\rho_\beta = \frac{\exp(-\beta H)}{\mathrm{Tr}(\exp(-\beta H))} \tag{7.1}$$

where $\beta=1/kT$, and T is the temperature. The density operator ρ_β shares a common eigenbasis with the Hamiltonian operator. We denote the energy eigenvectors by $\{\psi_i\}$ and the energy eigenvalues by $\{e_i\}$, i.e.,

$$H\psi_i = e_i\psi_i. \tag{7.2}$$

For the sake of convenience, we order the energy eigenvalues : $e_1 \le e_2 \le \dots \le e_i \le \dots$ We denote by $\{p_i\}$ the eigenvalues of the canonical distribution, i.e.,

$$\rho_\beta\psi_i = p_i\psi_i. \tag{7.3}$$

The ratio of two eigenvalues of the canonical distribution satisfies the relation

$$\frac{p_i}{p_1} = \exp\left(-\beta(e_i - e_1)\right) \tag{7.4}$$

We consider positive temperatures only, and let temperature T converge to zero. The inverse temperature β goes to infinity. The ratio of the eigenvalues of the canonical distribution given by Equation (7.4) converges to zero if $e_1<e_i$, and to unity if $e_1=e_i$. If the ground-energy state of the system is not degenerate, i.e., $e_1<e_2$, we conclude that p_1 converges to unity, and all other eigenvalues to zero. In other words, the canonical distribution converges to the projection operator onto the one-dimensional space spanned by the vector ψ_1. The entropy associated with a projection operator is zero. So we conclude that the entropy converges to zero as temperature goes to zero. Therefore, for petit systems with a non-degenerate ground-energy state the lowest value of entropy attained by the stable equilibrium states is zero.

Next, we investigate the case of a petit system whose ground-energy state has a degeneracy $n>1$, i.e. , $e_1=\dots=e_n<e_{n+1}$. Using Equation (7.4), it is straightforward to show

that, in the limit T=0, $p_1=\ldots=p_n=1/n$, and $p_{n+1}=\ldots=0$. Therefore, the entropy associated with the canonical distribution converges to k Log(n). In other words, the lowest value of entropy attained by the stable equilibrium states of the system is k Log(n).

To account for the existence of petit systems with degenerate ground energy states, the second part of the statement of the second law should be modified to read [Gyftopoulos and Beretta, 1991i]: *Starting from any state of a system it is always possible to reach a stable equilibrium state or a ground-energy state with arbitrarily specified values of amounts of constituents and parameters by means of a reversible weight process.*

The situation is more complicated, however, if we consider a system that admits fractional expectation values of amounts of constituents, i.e., a grand system. For the sake of simplicity, we consider a grand system A with only one type of constituent. To define the Hilbert space H associated with A, we consider petit systems A_j that share the same constituent, the same parameters, and the same values of parameters with system A but each system A_j has an integer value n_j of the amount of the constituent. We denote by H_j the Hilbert space associated with each system A_j. The Hilbert space of system A is the direct sum of these Hilbert spaces, i.e., $H=H_1 \oplus H_2 \oplus \ldots \oplus H_j \oplus \ldots$ Similarly, the Hamiltonian operator H of system A, is the direct sum of the Hamiltonian operators H_j associated with systems A_j, i.e.., $H=H_1 \oplus H_2 \oplus \ldots \oplus H_j \oplus \ldots$ The number of constituent of operator N of system A can be expressed as $N=n_1 I_1 \oplus n_2 I_2 \oplus \ldots \oplus n_j I_j \oplus \ldots$ where I_j is the identity operator on H_j.

The density operator corresponding to a stable equilibrium state of a grand system is given by the grand canonical distribution, i.e. ,

$$\rho_{\beta,\nu} = \frac{\exp(-\beta H - \nu N)}{Tr(\exp(-\beta H - \nu N))} \tag{7.5}$$

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where $\beta=1/kT$ and $\nu=-\mu/kT$. It is convenient to use a double index to denote the eigenvalues of the grand canonical distribution so that

$$H_j \psi_i^j = e_{ij} \psi_i^j \quad \text{and} \quad H \psi_i^j = e_{ij} \psi_i^j \tag{7.6}$$

$$N \psi_i^j = n_j \psi_i^j . \tag{7.7}$$

Without loss of generality, we can order the eigenvalues of the number of constituent operator N such that $n_1 < n_2 < \ldots$ Similarly, the eigenvalues of the Hamiltonian operator are ordered such that $e_{1j} \leq e_{2j} \leq \ldots$ for each value of j. For the sake of simplicity, we also assume that the ground energy state of each A is non-degenerate, i.e., $e_{1j} < e_{2j} \leq \ldots$ Furthermore, the density operator shares a common set of eigenvectors with H and N, i.e.,

$$\rho_{\beta,\nu} \psi_i^j = p_{ij} \psi_i^j \tag{7.8}$$

where $\{p_{ij}\}$ are the eigenvalues of the density operator.

Combining Equations (7.5) and (7.8), we find that the ratio of two eigenvalues of the density operator satisfies the relation

$$\frac{p_{ij}}{p_{kl}} = \exp\left(-\beta\left(e_{ij} - e_{kl}\right) - \nu\left(n_j - n_l\right)\right). \tag{7.9}$$

Given the values of the amount of constituent <N> and temperature T, the grand canonical distribution is uniquely determined, i.e., there exists a unique value of ν such that the expectation value of N matches the given value. We fix the value of <N> and let T goes to zero. It follows from Equation (7.9) that

$$\frac{p_{ij}}{p_{1j}} = \exp\left(-\beta\left(e_{ij} - e_{1j}\right)\right) = 0 \quad \forall i > 1 \tag{7.10}$$

Therefore, as T goes to zero, the only nonzero eigenvalues of the density operator are in the set $\{p_{1j}\}$. If the given value of the amount of constituent <N> is not an integer, at least two of the eigenvalues of the density operator are nonzero, because we must have

$$\langle N \rangle = \mathrm{Tr}\left(N\rho_{\beta,v}\right) = \sum_{j} n_j p_{1j} \tag{7.11}$$

and all n_j's are integer. Therefore, the value of entropy at zero temperature is nonzero, and is a function of <N>. Even if <N> is an integer that corresponds to a number of constituent eigenvalue n_j, it is not guaranteed that the entropy associated with the grand canonical distribution vanishes.

For grand systems, therefore, the lowest value of entropy attained by the stable equilibrium states is a function of the amount of constituent <N>, and in general is nonzero. The first implication of this observation is that the modification of the second law introduced to capture petit systems with degenerate ground-energy states is essential to account for the existence of grand systems.

However, for an arbitrary value of <N>, the existence of ground-energy states other than the stable equilibrium state with zero temperature remains unresolved. To show this point, we consider a state $\{\varepsilon, \rho_1\}$ of the system, such that the density operator is diagonal in energy representation and that the eigenvalues of the density operator are $p_1 = 1$ and $p_2 = \ldots = 0$. The expectation value of the number of constituent in this state is n_1, and the value of entropy is zero. According to the modified second law, starting from state $\{\varepsilon, \rho_1\}$ we should be able to reach either a stable equilibrium state or a ground-energy state with an arbitrarily specified values of <N> and parameters by means of a reversible weight process. Because in a reversible weight process the value of entropy

remains invariant, the entropy of the final state must be zero. We know that for non-integer values of <N>, there exists no stable equilibrium state with zero entropy, and therefore, the final state must be a ground-energy state. The ground-energy state has zero entropy, hence is a mechanical state, and the wave function associated with it must be a linear superposition of at least two wave functions belonging to different Hilbert spaces H_j. Such a state, however, has never been reported, suggesting that rules similar to superselection rules (see Jauch [1968]) should be established to restrict the superposition principle. More specifically, it appears that the linear superposition of two wave functions belonging to two different Hilbert spaces H_j is not an acceptable wave function. We have not been able to resolve this difficulty, and further investigation is necessary.

In this discussion, we have assumed that the convergence of a density operator implies the convergence of the corresponding value of the entropy, i.e.,

$$\text{if} \quad \rho_1 \rightarrow \rho_2 \quad \text{then} \quad S(\rho_1) \rightarrow S(\rho_2) \tag{7.12}$$

Even though this in not true in general, Wehrl [1978] showed that if the Hamiltonian operator of a system is such that $\exp(-\beta H) < \infty$ for all $\beta > 0$, Equation (7.12) holds true. In Section 4.4, we show that this condition is always satisfied in quantum thermodynamics, and therefore, we conclude that our assumption is valid.

We would like to remind that, this result is valid equally well in statistical quantum mechanics when the entropy of the system is represented by the von Neumann entropy.

7.2 Triple Points

In Section 3.2, we have introduced the entropy versus energy graph of the states of a system. In this graph the stable-equilibrium-states curve must be concave. In

Section 4.1, the concavity of the stable-equilibrium-states curve is one of the conditions that must be satisfied by the expression for entropy in Section 4.1. In Section B.3, we show that the von Neumann entropy not only satisfies this requirement, but the stable-equilibrium-states curve it implies is strictly concave. Therefore, there exists no interval of energy for which the slope of the curve remains constant. However, the behavior of many systems appears to contradict this conclusion.
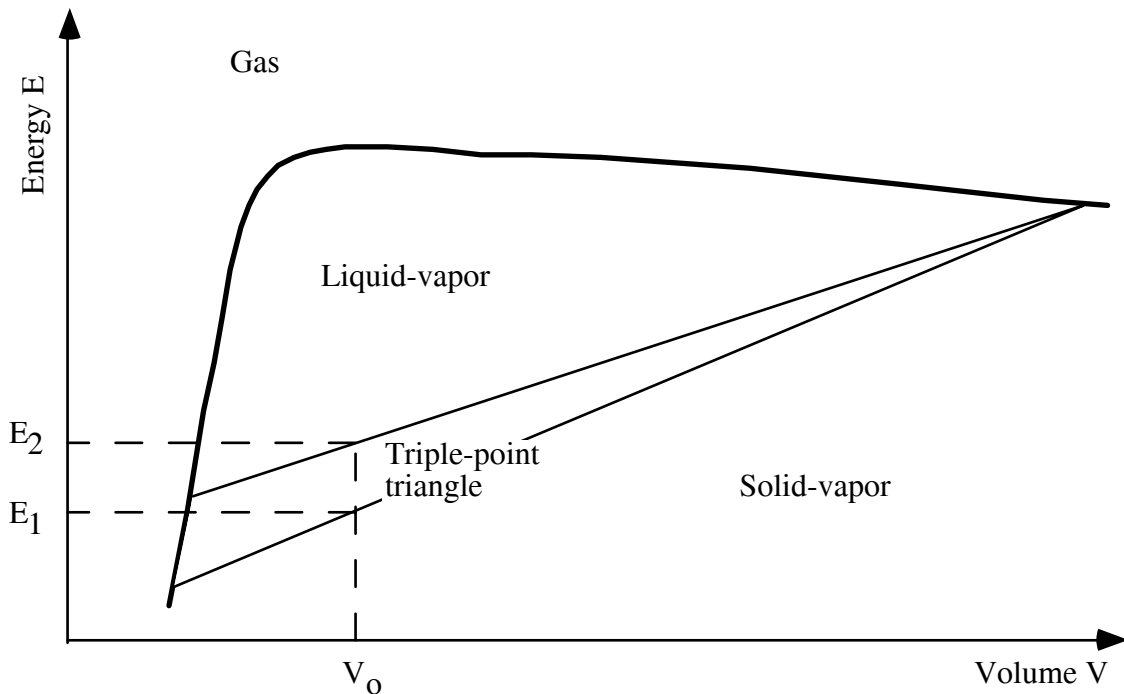

Figure 7.1 A typical energy versus volume diagram of a pure substance

Using the tabulated data for stable equilibrium states of a pure substance we can make a diagram of energy versus volume. For $<N>=1$ g, a typical diagram is shown in Figure 7.1. We choose the value of volume V_0 shown on the diagram, and denote by E_1 and E_2 the values of energies at which the vertical line passing through V_0 intercepts the triple point triangle. In the range of energy between E_1 and E_2, the substance passes through the triple point, i.e., all three phases (solid, liquid, vapor) co-exist in mutual stable equilibrium. It is a well-known property of the triple points of pure substances that

the temperature and pressure are independent of the fraction of different phases. Therefore, the entropy versus energy graph of the system has a constant slope between E_1 and E_2 which is in contradiction with the conclusion we have reached in Section B.3.

We would like to remind that this difficulty exists in statistical quantum mechanics as well, and that the same argument applies whenever three different phases (not necessarily solid-liquid-vapor) co-exist in mutual stable equilibrium. So far, we have not been able to provide a satisfactory explanation. The resolution of the difficulty requires a careful scrutiny of all the arguments related to triple points.

Chapter 8

8. Summary and Recommendations

The three purposes of this dissertation are to determine the mathematical expression for entropy, to establish which of the proposed equations of motion are satisfactory for quantum thermodynamics, and to provide experimental evidence for the validity of this equation.

We begin our investigation by reviewing the relation between mechanics and thermodynamics. We find that the only consistent relation is provided by a quantum theoretic (non-statistical) representation of thermodynamic concepts. In this representation the key idea is the existence of quantum states that involve irreducible - homogeneous - density operators ρ which satisfy both $\rho=\rho^2$ and $\rho \neq \rho^2$.

Next, we address the question of the mathematical expression for entropy. To answer this question, we establish a set of necessary conditions that need to be satisfied by entropy, and we investigate whether each mathematical expression for entropy proposed in the literature satisfies all these conditions. Among many of the proposed expressions, it turns out that only one - the von Neumann entropy - satisfies all the conditions.

Regarding the dynamical law, we specify a set of necessary conditions that need to be satisfied by this law, and investigate whether any of the equations of motion proposed in the literature are consistent with all these conditions. We find that only one equation is acceptable, and that is the Beretta equation. We determine, for the first time, a special class of solutions of the Beretta equation which can be used in describing many relaxation phenomena.

The third issue is the quest for conclusive and definitive experiments with systems having few degrees of freedom. To this end, we compare the results of two spin-relaxation experiments with the predictions of the Beretta equation. We show that these results are consistent with the Beretta equation.

Because the experiments in the literature were not intended to verify the validity of the Beretta equation, we should emphasize that the reported results are not sufficient to provide accurate quantitative comparisons. Accordingly, we suggest a variation of these experiments which, we believe, can give quantitative verification of quantum thermodynamics. The suggested experiment uses the same apparatus as the other two experiments.

In an effort to provide experimental validation of quantum thermodynamics, Beretta considered systems associated with finite-dimensional Hilbert spaces, and showed that his equation reduces to the phenomenological equations of irreversible thermodynamics. In this dissertation, for the first time, we show that Beretta's result can be generalized to systems with infinite dimensional Hilbert spaces, and can be expressed in a convenient form where the forces are temperature and chemical potential gradients.

Finally, we discuss two unresolved problems. The first problem relates to the value of entropy of stable equilibrium states with zero temperature. For grand systems, we conclude that the problem requires more careful consideration. The second problem relates to triple points of pure substances. We show that the existence of triple points requires refinement of the concepts used in the description of these points.

For future work, we suggest a specific spin-relaxation experiment which can provide a definitive validation of quantum thermodynamics.

We also suggest an investigation of the existence of ground-energy states of a grand system other than the zero temperature stable equilibrium state. Finally, the intriguing behavior of pure substances passing through triple-points, namely the invariance of the temperature over a range of values of energy requires further study.

Appendix A

This appendix is devoted to an investigation of the equations of motion proposed as an alternative to the Schrödinger equation. In Section A.1, we show that modifications of the Schrödinger equation, that maintain the linearity in ψ, imply a unitary time evolution. As a result, no increase in entropy can be achieved by using an equation of motion linear in ψ. In Section A.2, we present some of the nonlinear Schrödinger equations found in the literature. Difficulties encountered with these equations are explained. Most importantly, it is shown that the modified von Neumann equation corresponding to a nonlinear Schrödinger equation is ambiguous, and therefore the time evolution of a statistical state $\{\varepsilon,\rho\}$ is not uniquely determined by its initial value. We conclude that modifications of the Schrödinger equation involving nonlinear terms are unacceptable because they result in a statistical quantum mechanical theory which is non-deterministic.

A.1 Equation of Motion Linear in ψ

In the case of an isolated system, the set ε of instantaneous operators corresponding to independent observables remains invariant in time. Hence the time evolution of a state $\{\varepsilon,\psi\}$ is determined solely by that of ψ which in turn is governed by the equation of motion. Furthermore, in a deterministic theory, the state at any later instant of time is determined uniquely by the state at an earlier time. The simplest equation of motion possessing this feature has the following mathematical representation:

$$\frac{\partial \psi}{\partial t} = f(\varepsilon, \psi), \tag{A.1}$$

where $f(\varepsilon, \psi)$ is a function of the state $\{\varepsilon, \psi\}$. When the equation of motion is linear in ψ, Equation (A.1) becomes

$$\frac{\partial \psi}{\partial t} = L\psi, \qquad \text{(A.2)}$$

where L is a linear operator on the Hilbert space H independent of ψ. Because it is associated with probabilities, the state vector ψ must be normalized at all instants of time t:

$$< \psi, \psi >= 1 \;, \forall t. \qquad \text{(A.3)}$$

The time derivative of Equation (A.3) gives:

$$< \frac{\partial \psi}{\partial t}, \psi > + < \psi, \frac{\partial \psi}{\partial t} >= 0 \qquad \text{(A.4a)}$$

or, plugging Equation (A.2) into Equation (A.4a)

$$\langle L\psi, \psi \rangle + \langle \psi, L\psi \rangle = 0. \qquad \text{(A.4b)}$$

If L^* denotes the adjoint of the linear operator L, then the equation (A.4b) reduces to:

$$< \psi, L^* \psi > + < \psi, L\psi >=< \psi, \left(L + L^* \right)\psi >= 0. \qquad \text{(A.5)}$$

The linear operator $L+L^*$ is Hermitian. Equation (A.5) is valid for all ψ such that $\|\psi\|=1$. To any element Φ of the Hilbert space H there corresponds a unique ψ (with unit norm) such that

$$\Phi = \|\Phi\| \ \psi. \tag{A.6}$$

By virtue of Equation (A.6), Equation (A.5) is valid for $\forall \ \psi \ \ H$, and since the linear operator $L+L^*$ is Hermitian, $L+L^*$ is the null operator [Conway, 1985]:

$$L + L^* = 0 \ \text{ or } \ L = -L^*. \tag{A.7}$$

An operator L that satisfies Equation (A.7) is, by definition, an anti-Hermitian operator. Therefore,

$$L = iM, \tag{A.8}$$

where M is Hermitian. Hence, Equation (A.2) can be written as

$$\frac{\partial \psi}{\partial t} = iM\psi, \tag{A.9}$$

or, alternatively, in the projection operator $P_\psi = |\psi><\psi|$ representation

$$\frac{\partial P_\psi}{\partial t} = i\big[M, P_\psi\big]. \tag{A.10}$$

This general form of the equation is very similar to the Schrödinger equation. Therefore, there is not much room for improving the equation of motion if it is kept linear in ψ. Using the Hermiticity of M, it is straightforward to show that the time evolution implied by Equation (A.8) is unitary, even when M is time-dependent [Messiah, 1961].

A linear equation of motion yields a unitary time evolution, so the von Neumann entropy (Equation (3.11)) of the system is conserved. Furthermore, the conservation of energy in a closed system requires that the operators M and H commute, i.e., [H,M]=0. Indeed,

$$0 = \frac{d}{dt} < \psi, H\psi >=< \frac{\partial \psi}{\partial t}, H\psi > + < \psi, H\frac{\partial \psi}{\partial t} > \tag{A.11}$$

Using Equation (A.9) and the Hermiticity of M,

$$0 = \langle iM\psi, H\psi \rangle + \langle \psi, iHM\psi \rangle = -i\langle \psi, MH\psi \rangle + i\langle \psi, HM\psi \rangle \tag{A.12}$$

From Equations (A.12) and (A.6), it follows that:

$$< \psi, HM\psi > - < \psi, MH\psi >=< \psi, [H,M]\psi >= 0, \ \forall \psi \in H. \tag{A.13}$$

Since the Hilbert space H is complex, Equation (A.13) implies that [H,M]=0 [Conway, 1985].

A.2 Nonlinear Schrödinger Equations

In an attempt to describe dissipative quantum evolution, several nonlinear Schrödinger equations are proposed in the literature. Kostin [1972, 1975] suggested a modification to the Schrödinger involving a nonlinear logarithmic term

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\Delta + V \right)\psi - \frac{\gamma}{2}\left(\text{Log}\frac{\psi}{\psi^*} - \left\langle \text{Log}\frac{\psi}{\psi^*} \right\rangle \right)\psi, \tag{A.14}$$

where γ is a positive constant, and < **.** > denotes the expectation value. Schuch *et al* [1983, 1984a, b] proposed a similar equation

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\left(-\frac{\hbar^2}{2m}\Delta + V\right)\psi - \frac{\gamma}{2}\Big(Log(\psi) - \langle Log(\psi)\rangle\Big)\psi \,.$$

(A.15)

Gisin [1983a, b, 1986] studied the equation

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}H\psi - \gamma(A - \langle A\rangle)\psi \,,$$

(A.16)

where H is the Hamiltonian, and A is a Hermitian operator on H, including A=H.

A nonlinear Schrödinger equation with a "friction potential" involving expectation values of momentum and position has been proposed by Albrecht [1975], and Hasse [1975]. It is given by the relation

$$\frac{\partial \psi}{\partial t} = \frac{1}{i\hbar}\Big(H + \gamma W(\psi)\Big)\psi \,,$$

(A.17)

where $W(\psi) = (x - \langle x\rangle)(cp + (1 - c)\langle p\rangle) - ic\hbar/2$, and the constants γ and c are positive. For a damped harmonic oscillator, solutions of Equation (A.17) have been studied by Lange [1985].

All these nonlinear Schrödinger equations (Equations (A.14)-(A.17)) conserve the normalization of ψ. However, the value of energy is not conserved in all states. Therefore, these equations cannot satisfactorily describe dissipation in a closed system where the value of energy remains fixed while the value of entropy increases in time. Furthermore, Equations (A.14) and (A.15) are exclusively expressed in the position representation. Unless they can be generalized to a representation-free form, their validity would be limited to systems with a notion of position. As such, they cannot be

applied to spin systems. Similarly, the validity of Equation (A.17) is restricted because it contains the position operator.

The major difficulty encountered with a nonlinear Schrödinger equation is the non-uniqueness of the corresponding von Neumann equation. In order to to prove this assertion, we present first a peculiarity of statistical quantum mechanics regarding the decomposition of a statistical state into pure states. As first noted by Schrödinger [1936], this decomposition is non-unique unless the statistical state operator ρ is a projection . This is in strong contrast with the classical case where the decomposition is always unique.

Consider the statistical state $\{\varepsilon, \rho\}$, where ρ in a given representation is

$$\rho = \begin{bmatrix} 1/4 & 0 \\ 0 & 3/4 \end{bmatrix}. \tag{A.18}$$

This operator is not a projection. Hence it can be decomposed into projections in infinitely many different ways [Park, 1988]. For example, using the four pure states, either in vectorial representation $\{\varepsilon, \psi_1\}$ to $\{\varepsilon, \psi_4\}$, where

$$\psi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \ \psi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \ \psi_3 = \begin{bmatrix} \sqrt{2}/2 \\ \sqrt{2}/2 \end{bmatrix}, \ \psi_4 = \begin{bmatrix} -1/\sqrt{10} \\ 3/\sqrt{10} \end{bmatrix}, \tag{A.19}$$

or, equivalently, in the operator representation $\{\varepsilon, P_1\}$ to $\{\varepsilon, P_4\}$, where

$$P_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \ P_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \begin{bmatrix} 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix},$$

$$P_3 = \begin{bmatrix} \sqrt{2}/2 \\ \sqrt{2}/2 \end{bmatrix} \begin{bmatrix} \sqrt{2}/2 & \sqrt{2}/2 \end{bmatrix} = \begin{bmatrix} 1/2 & 1/2 \\ 1/2 & 1/2 \end{bmatrix},$$

$$P_4 = \begin{bmatrix} -1/\sqrt{10} \\ 3/\sqrt{10} \end{bmatrix} \begin{bmatrix} -1/\sqrt{10} & 3/\sqrt{10} \end{bmatrix} = \begin{bmatrix} 1/10 & -3/10 \\ -3/10 & 9/10 \end{bmatrix}, \tag{A.20}$$

we can write ρ in the forms:

$$\rho = \frac{1}{4}P_1 + \frac{3}{4}P_2, \tag{A.21a}$$

$$\rho = \frac{3}{8}P_3 + \frac{5}{8}P_4. \tag{A.21b}$$

The two forms yield different time evolutions of the statistical operator ρ given by Equation (A.18). To prove this point, we investigate Equation (A.16) with A=H only, even though the proof applies equally well to any other nonlinear Schrödinger equation. First, we define the system and evaluate the time evolution of a pure state of the system according to Equation (A.16).

We consider a two-level system with the Hamiltonian operator (matrix) in the energy representation

$$H = \begin{bmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{bmatrix}, \tag{A.21}$$

where $\varepsilon>0$. For A=H, Equation (A.16) implies that

$$\frac{\partial \psi_1}{\partial t} = \frac{\partial \psi_2}{\partial t} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \text{ and } \frac{\partial P_1}{\partial t} = \frac{\partial P_2}{\partial t} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix}, \tag{A.22}$$

i.e., that $\{\varepsilon,\psi_1\}$ and $\{\varepsilon,\psi_2\}$ are stationary states. Actually, they are the only stationary states, because Equation (A.16) implies

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$$\frac{d\langle H\rangle}{dt} = -2\gamma\left(\langle H^2\rangle - \langle H\rangle^2\right) = -2\gamma(\Delta H)^2 , \qquad (A.23)$$

$(\Delta H)^2$ is always non-negative and equals to zero only if ψ is an energy eigenvector. For initial conditions ψ other than ψ_2, Equation (A.23) shows that the solution of Equation (A.16) tends always to ψ_1 and that Equation (A.16) does not preserve energy.

Next, we evaluate the time evolution of this system initially known to be described by the statistical state $\{\varepsilon,\rho\}$ given by Equation (A.18) in energy representation. If the statistical state is conceived of as the mixture of pure states $\{\varepsilon,\psi_1\}$ and $\{\varepsilon,\psi_2\}$ given by Equation (A.21a), using Equation (A.22), we conclude that it does not change with time. However, if it is conceived of as the mixture of pure states $\{\varepsilon,\psi_3\}$ and $\{\varepsilon,\psi_4\}$ given by Equation (A.21b), it eventually converges to $\{\varepsilon,P_1\}$ because both pure states converge to $\{\varepsilon,\psi_1\}$.

Because the time evolution of the statistical state operator depends on its decomposition into projections, there cannot exist a unique equation of motion in statistical quantum mechanics similar to the von Neumann equation (Equation 2.10). Therefore, we conclude that the quantum dissipative dynamics cannot be satisfactorily described by a nonlinear Schrödinger equation. We would like to emphasize that, the same difficulty does not arise in the case of the Schrödinger equation, where the linearity of the equation guarantees that the time evolution of the statistical state operator is independent of its decomposition into projections.

Appendix B

In this appendix, we investigate the properties of several expressions for entropy presented in Section 4.1. We begin by showing the deficiencies of the Hartley entropy I_H and the infinite norm entropy I_∞ given by Equations (4.2) and (4.5) respectively. Next, we show that the von Neumann entropy (Equation (4.1)) satisfies Conditions 6 and 7, and the Rényi entropy (Equation (4.4)) Conditions 5, 6 and 7 specified in Section 4.2.

B.1 Deficiency of the Hartley Entropy

To show the deficiency of the Hartley entropy (Equation (4.2))

$$I_H = k \; \text{Log}\big(N(\rho)\big) \tag{B.1}$$

where $N(\rho)$ is the the number of positive eigenvalues of ρ, we consider a two-level system, i.e., dim $(H)=2$. Mechanical states $\{\varepsilon,\rho\}$ (i.e., where ρ is a projection) have $I_H(\rho)=k \, \text{Log}(1)=0$. All the other states have $I_H(\rho)=k \, \text{Log}(2)$. Without loss of generality, we can assume

$$H = \begin{bmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{bmatrix} \tag{B.2}$$

where $\varepsilon>0$. Given the value of energy $<H>=0$, let us find the stable equilibrium state. This state must have the maximum value of entropy among the states which have energy 0 (as explained in Section 3.1.2). However, for δ a complex number such that $|\delta|<1/2$, all the states $\{\varepsilon,\rho_\delta\}$ with ρ_δ in the energy representation given by the matrix

$$\rho_\delta = \begin{bmatrix} 1/2 & \delta^* \\ \delta & 1/2 \end{bmatrix} \tag{B.3}$$

have energy 0 and entropy k Log(2). It follows that for the given value of energy, many states share the largest value of entropy, i.e., the Hartley entropy violates Condition 5 specified in Section 4.1.

B.2 Deficiency of the Infinite Norm Entropy

To show the deficiency of the infinite norm entropy, we consider the two-level system described in Section B.1. If the infinite norm entropy (Equation 4.5)

$$I_\infty = -k \ \text{Log} \|\rho\|_\infty \tag{B.4}$$

where $\|\rho\|_\infty = p_{max}$ is the largest eigenvalue of ρ, is the expression for entropy, we will show that the curve of the stable equilibrium states on the entropy versus energy graph is neither smooth nor concave. To this end, we carry out the maximization problem first. In the 2-level system under consideration, $\|\rho\|_\infty = p_1$, where p_1 is the largest eigenvalue of the density operator ρ, hence in order to determine the stable equilibrium states we need to maximize p_1 for a given value of energy.

Claim: The density operators corresponding to stable equilibrium states are diagonal in energy representation.

Proof: Any density operator ρ in energy representation is of the form

$$\rho = \begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix}, \tag{B.5}$$

where $0 \le x \le 1$ and δ is a complex number such that $|\delta| \le (x - x^2)$. Eigenvalues p_1 and p_2 of the density operator ρ, satisfy

$$p_1 + p_2 = 1 \quad \text{and} \quad p_1 \cdot p_2 = \text{Det}(\rho) = |\rho| = x - x^2 - |\delta|^2, \tag{B.6}$$

hence they are the solutions of the quadratic equation

$$p^2 + p - |\rho| = 0. \tag{B.7}$$

We need to maximize the largest eigenvalue p_1 of ρ, for a given value of energy $<H>$. However, $<H>$ uniquely determines x, because

$$\langle H \rangle = \text{Tr}(H\rho) = \text{Tr}\left(\begin{bmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{bmatrix} \begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix} \right) = \varepsilon(1 - 2x). \tag{B.8}$$

Therefore, we have to evaluate the value of δ which yields the largest p_1, subject to the condition that the value of energy is $<H>$. From Equation (B.7) we find that

$$p_1 = \frac{1}{2} \left(1 + \sqrt{1 - 4|\rho|} \right). \tag{B.9}$$

Hence p_1 is maximum if $|\rho|=x-x^2-|\delta|^2$ is minimum, i.e., if $|\delta|=0$.

Because the density operator corresponding to a stable equilibrium state is diagonal in the energy representation, we conclude that

$$p_1 = \begin{cases} x & \text{if } x \ge 1/2 \\ 1-x & \text{if } x < 1/2. \end{cases} \tag{B.10}$$

From Equation (B.8) we find that $x = \dfrac{1}{2}\left(1 - \dfrac{\langle H \rangle}{\varepsilon}\right)$, and

$$p_1 = \begin{cases} \dfrac{1}{2}\left(1 - \dfrac{\langle H \rangle}{\varepsilon}\right) & \text{if } \langle H \rangle \leq 0 \\[3mm] \dfrac{1}{2}\left(1 + \dfrac{\langle H \rangle}{\varepsilon}\right) & \text{if } \langle H \rangle > 0. \end{cases} \qquad (B.11)$$

Because $I_\infty = -k\,\text{Log}(p_1)$, we can now make a graph of the stable equilibrium states curve on the entropy-energy plane (Figure B.1) which is neither smooth nor concave. Therefore, we conclude that I_∞ violates Condition 6 specified in Section 4.1.
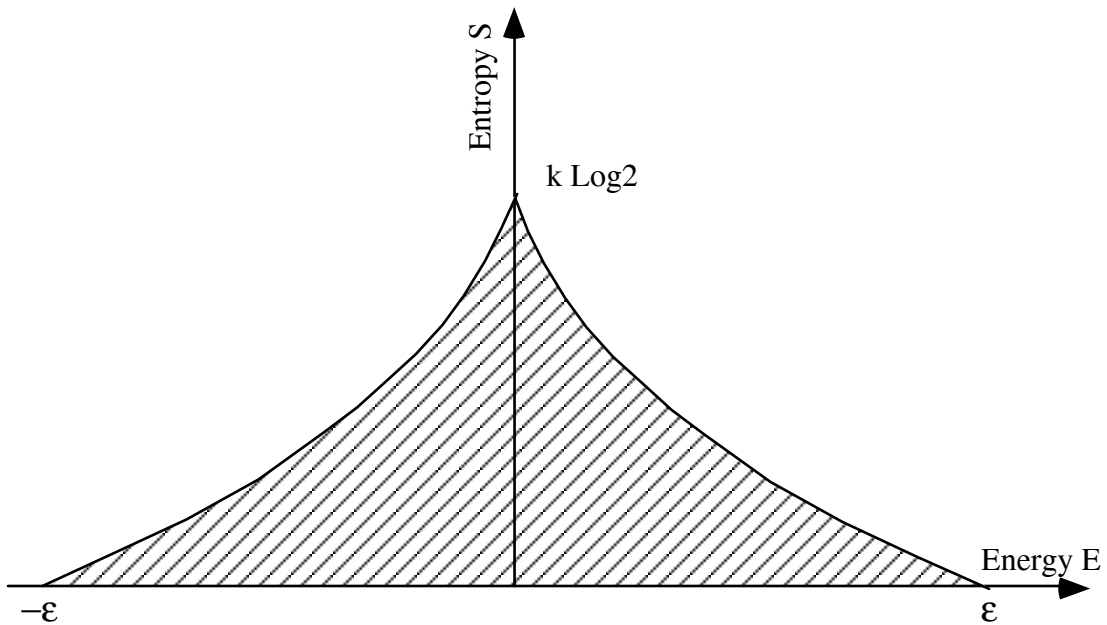

Figure B.1 Energy versus infinite norm entropy graph

B.3 The von Neumann Entropy

In this section we show that the von Neumann entropy (Equation 4.1)

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$$I_v = -k \ Tr\bigl(\rho \ Log(\rho)\bigr)$$ (B.12)

satisfies Conditions 6 and 7 specified in Section 4.2. It is shown by Katz [1967] that the von Neumann entropy admits a unique maximum for a given value of energy, and given values of the amounts of constituents and parameters. Katz also shows that the density operator ρ_β corresponding to a stable equilibrium state is diagonal in the energy representation, and that for a petit system, it has the form given by Equation (4.8)

$$\rho_\beta = \frac{\exp(-\beta H)}{Tr\bigl(\exp(-\beta H)\bigr)}, \quad \beta = \frac{1}{kT}$$ (B.13)

where T is the temperature at that state, and H is the Hamiltonian operator. Because of its simplicity, we consider a petit system. However, the proofs that follow are valid for any system.

To show that the stable-equilibrium-states implied by the von Neumann entropy is concave, i.e., that I_v satisfies Condition 6, first we need to introduce a more appropriate notation. We denote by $\{\varepsilon,\rho_1\}$ and $\{\varepsilon,\rho_2\}$ the stable equilibrium states having energies $<H>_1$ and $<H>_2$, respectively, and by $I_v(\rho)$ the entropy of state $\{\varepsilon,\rho\}$. Given a value of energy $<H>$ between $<H>_1$ and $<H>_2$, there exists a unique number $\lambda>0$, such that $<H>=\lambda<H>_1+(1-\lambda)<H>_2$. If $\{\varepsilon,\rho_\lambda\}$ denotes the stable equilibrium state of energy $<H>$, the concavity of the curve of stable equilibrium states on the entropy versus energy plane is equivalent to

$$I_v\bigl(\rho_\lambda\bigr) \ge \lambda I_v\bigl(\rho_1\bigr) + (1-\lambda)I_v\bigl(\rho_2\bigr), \ \forall \ 0<\lambda<1.$$ (B.14)

We define the operator $\rho_{\lambda 3}=\lambda\rho_1+(1-\lambda)\rho_2$ which is easily checked to be a density operator. From the linearity of the Hamiltonian operator, the energy of the system in

state $\{\varepsilon, \rho_{\lambda 3}\}$ is $\langle H \rangle = \lambda \langle H \rangle_1 + (1-\lambda)\langle H \rangle_2$. Furthermore, $\rho_{\lambda 3}$ is diagonal in energy representation, because both ρ_1 and ρ_2 are diagonal in this representation. If $\{p_{1i}\}$ and $\{p_{2i}\}$ denote the eigenvalues of ρ_1 and ρ_2, respectively, then the eigenvalues $\{p_{3i}\}$ of $\rho_{\lambda 3}$ satisfy

$$p_{3i} = \lambda p_{1i} + (1-\lambda)p_{2i}, \ \forall i. \tag{B.15}$$

If $f(x)=-k \, xLog(x)$, with the convention that $f(0)=0$, it is easy to show that $f(x)$ is concave in the region $0 \le x \le 1$, and that

$$I_v(\rho) = \sum_i f(p_i), \tag{B.16}$$

where $\{p_i\}$ are the eigenvalues of ρ. Using the concavity of $f(x)$, and Equations (B.15) and (B.16), we find that

$$I_v(\rho_{\lambda 3}) > \lambda I_v(\rho_1) + (1-\lambda)I_v(\rho_2). \tag{B.17}$$

Because both $\rho_{\lambda 3}$ and ρ_λ correspond to the same value of energy $\langle H \rangle$, by definition

$$I_v(\rho_\lambda) \ge I_v(\rho_{\lambda 3}), \tag{B.18}$$

where the equality holds hold only if $\rho_\lambda = \rho_{\lambda 3}$. Combining relations (B.17) and (B.18), we show that Equation (B.14) is indeed satisfied. Therefore the stable-equilibrium-states curve implied by the von Neumann entropy is concave, i.e., I_v conforms to Condition 6 specified in Section 4.1.

Regarding Condition 7, we prove it for petit systems, even though the proof applies to any system. If H_A and H_B denote the Hamiltonian operators of two

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independent petit systems A and B, respectively, the Hamiltonian of the composite system is $H_{AB}=H_A \otimes I_B + I_A \otimes H_B$, where I_A and I_B are the identity operators on H_A and H_B, respectively. Thus, any stable equilibrium state of the composite system is of the form $\{\varepsilon_A \cup \varepsilon_B, \rho_{AB}\}$, where

$$\rho_{AB} = \frac{\exp(-\beta H_{AB})}{Tr(\exp(-\beta H_{AB}))}. \tag{B.19}$$

It is easy to verify that $\rho_{AB}=\rho_A \otimes \rho_B$, where $\{\varepsilon, \rho_A\}$ and $\{\varepsilon, \rho_A\}$ are the stable equilibrium states of A and B, respectively, each corresponding to the same value of $\beta=1/kT$. The temperature equality of A and B implies that the composite system is in a stable equilibrium state. We conclude that the von Neumann entropy satisfies Condition 7 specified in Section 4.1.

B.4 Deficiency of the Rényi Entropies

In this section we provide the proofs that the Rényi entropy of order α (Equation (4.4))

$$I_\alpha = \frac{k}{1-\alpha} Log\left(Tr\left(\rho^\alpha\right)\right) \tag{B.20}$$

where $\alpha>0$, $\alpha \neq 1$, satisfies Conditions 5 and 6 specified in Section 4.1 but fails to comply with Condition 7. First, we determine the stable equilibrium states implied by I_α. This is done by maximizing the value of entropy I_α, for a given value of energy, and the given values of amounts of the constituents and parameters. To simplify the notation, we solve the problem only for a petit system. The generalization to any system is straightforward.

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Given the amounts of constituents and the parameters, the Hamiltonian H is uniquely determined. Given a value of energy <H>, we search for the state $\{\epsilon,\rho_\gamma\}$ which maximizes I_α. Because the logarithm is a monotonic function of the argument, this is equivalent to maximizing $Tr(\rho^\alpha)$. Here, we use the ideas of Katz [1967] who solves the same problem for the von Neumann entropy.

Because this is a constrained maximization problem, the method of Lagrange multipliers is appropriate. We begin by fixing the value of α. There are two constraints imposed on ρ: $Tr(\rho)=1$ and $Tr(H\rho)=<H>$. Hence, we define the new function to be maximized as $I(\rho)=Tr(\rho^\alpha)-\alpha\lambda-\alpha\gamma<H>$, where λ and γ are the Lagrange multipliers. We have two degrees of freedom: changing the eigenvalues and the orientation of the eigenvectors of the density operator ρ. The latter change results in ρ_γ being diagonal in the energy representation.

Proof: The orientation of the eigenvectors of ρ can be changed without altering its eigenvalues by means of a unitary transformation. Such a transformation can be written in the form

$$d\rho = i[W,\rho]d\omega, \qquad (B.21)$$

where W is a Hermitian operator, ω a parameter, and $d\rho$ the change in ρ due to a small change $d\omega$ in the parameter. Hence, the change in $I(\rho)$ due to a small change in ω, is given by the relation

$$dI = Tr\left((\rho + d\rho)^\alpha\right) - \alpha\gamma Tr\left(H(\rho + d\rho)\right) - Tr\left(\rho^\alpha\right) + \alpha\gamma Tr(H\rho) \qquad (B.22)$$

Because in a unitary transformation the eigenvalues remain invariant, Equation (B.22) reduces to

$$dI = -\alpha\gamma Tr(Hd\rho). \tag{B.23}$$

Substituting Equation (B.21) into Equation (B.23), we get

$$dI = i\alpha\gamma Tr(H[\rho, W])d\omega. \tag{B.24}$$

The function $I(\rho)$ is maximized when ρ is a stationary point, i.e., for every Hermitian operator W, $\dfrac{dI}{d\omega} = 0$. Choosing W=i$\alpha\gamma$[H,ρ] and using well-known properties of the trace operation, we transform Equation (B.24) into the relation

$$\frac{dI}{d\omega} = (\alpha\gamma)^2 Tr([H,\rho]^2) = 0. \tag{B.25}$$

Because $[H,\rho]^2$ is a non-negative definite Hermitian operator, its trace vanishes if and only if $[H,\rho]=0$. Therefore, $I(\rho)$ is maximized when ρ commutes with H.

Next, we maximize the value of $I(\rho)$ by changing the eigenvalues of ρ. If $\{p_i\}$ denote the eigenvalues of ρ, and $\{\varepsilon_i\}$ the eigenvalues of H, we find that

$$I(\rho) = \sum_i p_i{}^{\alpha} - \alpha\lambda \sum_i p_i - \alpha\gamma \sum_i \varepsilon_i p_i. \tag{B.26}$$

because ρ_γ must be diagonal in the energy representation. This expression is maximized when ρ is a stationary point, i.e., $\dfrac{\partial I}{\partial p_i} = 0$. Hence, we get

$$0 = \alpha p_i{}^{(\alpha-1)} - \alpha\lambda - \alpha\gamma\varepsilon_i \Rightarrow p_i = (\lambda + \gamma\varepsilon_i)^{1/(\alpha-1)} \tag{B.27}$$

or, alternatively Equation (4.9)

$$\rho_\gamma = (\lambda + \gamma H)^{1/(\alpha-1)}.$$ (B.28)

This result shows that, for given values of energy, amounts of constituents, and parameters, one and only state has the largest value of the Rényi entropy. In other words, the Rényi entropy satisfies Condition 5. Furthermore, with a little algebra, we can show that

$$\gamma = \frac{1-\alpha}{\alpha kT} \exp\left(\frac{(1-\alpha)}{k}S\right),$$ (B.29)

where T is the temperature, and $S = I_\alpha(\rho_\gamma)$, i.e., the entropy of the stable equilibrium state $\{\varepsilon, \rho_\gamma\}$.

Next, we show that the Rényi entropy satisfies Condition 6 for values of $0 < \alpha < 1$, i.e., that the stable-equilibrium-state curve it implies is concave. Again we consider the stable equilibrium states $\{\varepsilon, \rho_1\}$ and $\{\varepsilon, \rho_2\}$ of a petit system, having the values of energy $\langle H \rangle_1$ and $\langle H \rangle_2$ respectively. The proof is similar to that for the von Neumann entropy given in Section (B.3), and therefore we use the same notation. Given a value $\langle H \rangle$ between $\langle H \rangle_1$ and $\langle H \rangle_2$, there exists a unique $0 < \lambda < 1$ such that $\langle H \rangle = \lambda \langle H \rangle_1 + (1-\lambda) \langle H \rangle_2$. Hence, what we need to show is a variation of Equation (B.14)

$$I_\alpha(\rho_\lambda) \geq \lambda I_\alpha(\rho_1) + (1-\lambda) I_\alpha(\rho_2), \ \forall \ 0 < \lambda < 1.$$ (B.30)

Because both ρ_1 and ρ_2 are diagonal in the H representation, so is $\rho_{\lambda 3} = \lambda \rho_1 + (1-\lambda) \rho_2$. The eigenvalues $\{p_{i3}\}$ of $\rho_{\lambda 3}$ satisfy Equation (B.15). If $g(x) = x^\alpha$, then

$$J(\rho) = \exp\left(\frac{1-\alpha}{k} I_\alpha(\rho)\right) = \sum_i g(p_i).$$ (B.31)

In the interval $0 \leq x \leq 1$ and for $0 < \alpha < 1$, $g(x)$ is concave. Using Equation (B.15), we get

$$g(p_{3i}) > \lambda g(p_{1i}) + (1 - \lambda)g(p_{2i}). \tag{B.32}$$

Combining Equations (B.31) and (B.32), we obtain

$$J(\rho_{\lambda 3}) > \lambda J(\rho_1) + (1 - \lambda)J(\rho_2). \tag{B.33}$$

The inverse of the relation given in Equation (B.31) is

$$I_\alpha(\rho) = \frac{k}{1 - \alpha} \text{Log}(J(\rho)). \tag{B.34}$$

Because the logarithm is a monotonic function, Equations (B.33) and (B.34) imply

$$I_\alpha(\rho_{\lambda 3}) > \frac{k}{1 - \alpha} \text{Log}(\lambda J(\rho_1) + (1 - \lambda)J(\rho_2)). \tag{B.35}$$

Finally, we use the concavity of the logarithm to get

$$I_\alpha(\rho_{\lambda 3}) > \lambda I_\alpha(\rho_1) + (1 - \lambda)I_\alpha(\rho_2). \tag{B.36}$$

Because both ρ_λ and $\rho_{\lambda 3}$ correspond to same energy value <H>, by definition

$$I_\alpha(\rho_\lambda) \geq I_\alpha(\rho_{\lambda 3}), \tag{B.37}$$

where the equality holds only if $\rho_\lambda = \rho_{\lambda 3}$. Equations (B.36) and (B.37) together show that Equation (B.30) is satisfied. Accordingly, the stable-equilibrium-state curve implied by the Rényi entropy, for $0 < \alpha < 1$, is concave, i.e., the I_α complies with condition 6.

Next, we prove that the Rényi entropy does not satisfy Condition 7, i.e., if the expression for entropy is I_α, the stable equilibrium state of a composite of two independent systems A and B is not a mutual stable equilibrium state of subsystems A and B. To this end, we consider the composite system A+B of two independent petit systems A and B. The Hilbert space of the composite system is $H_A \otimes H_B$ and its Hamiltonian $H_{AB} = H_A \otimes I_B + I_A \otimes H_B$, where I_A and I_B are the identity operators on H_A and H_B, respectively. By virtue of Equation (B.28), any equilibrium state of the composite is of the form $\{\varepsilon_A \cup \varepsilon_B, \rho_{\gamma AB}\}$, where

$$\rho_{\gamma AB} = (\lambda + \gamma H_{AB})^{1/(\alpha-1)}. \tag{B.38}$$

The operator $\rho_{\gamma AB}$ does not represent a state for which A and B are in mutual stable equilibrium. Indeed, if $\{\varepsilon_A, \rho_{\gamma A}\}$ and $\{\varepsilon_B, \rho_{\gamma B}\}$ denote the stable equilibrium states of A and B, respectively, where

$$\rho_{\gamma A} = (\lambda_A + \gamma_A H_A)^{1/(\alpha-1)}, \text{ and } \rho_{\gamma B} = (\lambda_B + \gamma_B H_B)^{1/(\alpha-1)}, \tag{B.39}$$

in general there exists no set of values $\{\lambda_A, \gamma_A, \lambda_B, \gamma_B,\}$ such that $\rho_{\gamma AB} = \rho_{\gamma A} \otimes \rho_{\gamma B}$.

Proof: If $\{\varepsilon_i\}$ and $\{e_j\}$ denote the eigenvalues of H_A and H_B, respectively, the eigenvalues of H_{AB} are $\{\varepsilon_i + e_j\}$. Similarly, if $\{p_i\}$ and $\{q_j\}$ denote the eigenvalues of $\rho_{\gamma A}$ and $\rho_{\gamma B}$, respectively, the eigenvalues of $\rho_{\gamma A} \otimes \rho_{\gamma B}$ are $\{p_i q_j\}$. Using a double index, we denote the eigenvalues of $\rho_{\gamma AB}$ by $\{r_{ij}\}$.

We prove the claim by contradiction. To every value of γ, there corresponds a unique stable equilibrium state of the composite system (note that, we are not free to

choose λ arbitrarily, because of the normalization requirement of a density operator). Similarly, the stable equilibrium states of A and B depend solely on γ_A and γ_B respectively. If $\rho_{\gamma AB} = \rho_{\gamma A} \otimes \rho_{\gamma B}$, then

$$\left(\lambda + \gamma\left(\varepsilon_i + e_j\right)\right)^{1/(\alpha-1)} = r_{ij} = p_i q_j = \left[\left(\lambda_A + \gamma_A \varepsilon_i\right)\left(\lambda_B + \gamma_B e_j\right)\right]^{1/(\alpha-1)}, \qquad (B.40)$$

for all values of i and j. Because dim(H)≥2 in any system, there are at least four different combinations of i and j. However, there are only two independent variables, γ_A and γ_B. Hence, in general Equation (B.40) cannot be satisfied and we conclude that Rényi entropy violates Condition 7 specified in Section 4.1.

Appendix C

In this appendix, we investigate three different equations of motion proposed in the literature. The deficiencies of the Park-Simmons equations in quantum thermodynamics are shown for the first time. The deficiency of the Lindblad equation is proven based on an argument first given by Beretta. Finally, we show for the first time that the solution of the Beretta equation with arbitrary initial states exists and is unique for any system, and give the general rule of how the Beretta equation of a composite system is determined, when the time evolution of the independent subsystems obey their respective Beretta equation.

C.1 The Lindblad Equation

Here, we present a version of the Lindblad equation for a two-level system. Contrary to the general case, this equation conserves the value of energy, hence satisfies Condition 3 established in Section 5.1. We also show that this equation complies with the condition of the nondecrease of entropy (Condition 4). The Hamiltonian operator H (Equation (B.1)) and the density operator ρ (Equation (B.3)) of the two-level system are:

$$H = \begin{bmatrix} -\varepsilon & 0 \\ 0 & \varepsilon \end{bmatrix}$$

(C.1)

$$\rho = \begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix}$$

(C.2)

where $\varepsilon > 0$, $0 \leq x \leq 1$, and δ is a complex number such that $|\delta| \leq (x-x^2)$. We consider the Lindblad equation (Equation (5.4)) for n=1, and V specified by

$$V_1 = V = \begin{bmatrix} -\lambda & 0 \\ 0 & \lambda \end{bmatrix} \tag{C.3}$$

in the energy representation, where $\lambda > 0$. Clearly, $[H,V]=0$, $V=V^*$, and $V^*V=\lambda^2 I$, where I is the identity. Hence, (5.4) reduces to

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H,\rho] + V\rho V - \lambda^2 \rho. \tag{C.4}$$

Using the cyclic permutability of the trace operation, and Equation (C.3), we can verify that $Tr(HV\rho V)=Tr(VHV\rho)=Tr(VVH\rho)=\lambda^2 Tr(IH\rho)=\lambda^2 <H>$. Hence

$$\frac{d\langle H \rangle}{dt} = Tr\left(H \frac{\partial \rho}{\partial t} \right) = Tr(HV\rho V) - \lambda^2 \langle H \rangle = 0 \tag{C.5}$$

which shows that the equation (C.4) is energy conserving. Furthermore, with a little algebra Equation (C.4) can be written in the form of

$$\frac{d}{dt}\begin{bmatrix} x & \delta^* \\ \delta & 1-x \end{bmatrix} = \frac{2\varepsilon}{i\hbar}\begin{bmatrix} 0 & -\delta^* \\ \delta & 0 \end{bmatrix} - 2\lambda^2\begin{bmatrix} 0 & \delta^* \\ \delta & 0 \end{bmatrix} \tag{C.6}$$

which can be easily solved for x and δ as a function of time. If at t=0, the density operator is given Equation (C.2), the solution in energy representation at any later instant of time t is

$$\rho(t) = \begin{bmatrix} x & \gamma^*(t) \\ \gamma(t) & 1-x \end{bmatrix} \tag{C.7}$$

where $\gamma(t) = \exp\left(\left(-2\lambda^2 + \dfrac{2\varepsilon}{i\hbar}\right)t\right)\delta$. Once this solution is determined, it is also easy to verify that the entropy is a monotone non-decreasing function of time, hence Equation (C.4) satisfies Condition 4. It is also clear that the solution $\rho(t)$ of Equation (C.4) eventually becomes diagonal in energy representation. In a two-level system, every density operator diagonal in the energy representation corresponds to a stable equilibrium state, hence Equation (C.4) takes every state to the stable equilibrium state having the same energy, i.e., describes an evolution towards the equilibrium.

As mentioned in Section 5.3, the general Lindblad equation does not satisfy Conditions 5, 6 and 9 established in Section 5.1. To show that, we denote by $\{p_i\}$ and $\{\psi_i\}$ the instantaneous eigenvalues and eigenvectors of ρ, respectively, and the element in the ith row and j^{th} column of V_n in ρ representation by V_n^{ij}, i.e.,

$$V_n^{ij} = \langle \psi_i | V_n | \psi_j \rangle. \tag{C.8}$$

Next we determine the time evolution of the eigenvalues $\{p_i\}$ of the density operator ρ. It is straightforward to verify that

$$\frac{dp_i}{dt} = \langle \psi_i | \frac{\partial \rho}{\partial t} | \psi_i \rangle = \sum_n \left(\sum_j \left(p_j |V_n^{ij}|^2 \right) - p_i \sum_k \left(|V_n^{ki}|^2 \right) \right). \tag{C.9}$$

If initially $p_i = 0$, then Equation (C.9) reduces to

$$\frac{dp_i}{dt} = \sum_n \left(\sum_j \left(p_j |V_n^{ij}|^2 \right) \right) \geq 0 \tag{C.10}$$

which shows that the Lindblad equation preserves the non-negative definiteness of the density operator only in the forward direction in time. We claim that there exists density

operators for which the inequality is strict, i.e., $\dfrac{dp_i}{dt} > 0$ and $p_i = 0$. Indeed, for a given set

of eigenvectors $\{\psi_i\}$, if $p_1 = 1$, $p_k = 0$, and $\dfrac{dp_k}{dt} = 0 \;\; \forall k \neq 1$, from Equation (C.10) we

get

$$\sum_n \left| V_n^{k1} \right|^2 = 0 \;\; \forall k \neq 1 . \tag{C.11}$$

Moreover, repeating the same argument for $p_2 = 1$, $p_k = 0$, and $\dfrac{dp_k}{dt} = 0 \;\; \forall k \neq 2$, for

$p_3 = 1,...$ we conclude that

$$\left| V_n^{ij} \right| = 0 \;\; \forall i \neq j . \tag{C.12}$$

Equations (C.11) and (C.12) implies that Equation (C.9) reduces to

$$\frac{dp_i}{dt} = \sum_n \left(p_i \left| V_n^{ii} \right|^2 - p_i \left| V_n^{ii} \right|^2 \right) = 0 . \tag{C.13}$$

However, this would imply that the time evolution is unitary, because the eigenvalues $\{p_i\}$ of the density operator are time independent. In other words, the Lindblad equation reduces to the von Neumann equation.

Therefore, without loss of generality we can assume that there exists a projection operator, such that $p_1 = 1$ and $\dfrac{dp_2}{dt} > 0$. However, if this were the case, as pointed out by Beretta [1982], the rate of entropy generation becomes infinite, i.e.,

$$\frac{d\langle S \rangle}{dt} = -k \sum_i \frac{dp_i}{dt} \text{Log}(p_i) = +\infty , \text{ because } \frac{dp_2}{dt} \text{Log}(p_2) = -\infty . \tag{C.14}$$

Because the von Neumann equation preserves the entropy, Equation (C.14) clearly indicates that for pure states, the Lindblad equation does not reduce, even as an approximation, to the von Neumann equation. Moreover, the existence of mechanical states which are extremely dissipative and unstable is also in contradiction with our experimental observations. Hence, the Lindblad equation violates Conditions 6 and 9.

Furthermore, the existence of a density operator with eigenvalue $p_2=0$ and $\frac{dp_2}{dt} > 0$ is in contradiction with the determinism principle, because the state of the system in the past cannot be established from the Lindblad equation as the non-negative definiteness of the density operator is not preserved in the negative direction in time. Therefore, we conclude that the Lindblad equation violates Condition 5 in addition to Conditions 6 and 9, and is not acceptable.

C.2 The Park-Simmons Equation

Here we present the proof that the Park-Simmons equation (Equation (5.8)) violates Conditions 5, 6 and 9 specified in Section 5.1. The arguments are identical to the case of the Lindblad equation. We show the existence of mechanical states in which the rate of entropy generation is infinite. However, no such state has been reported so far, and clearly existence of such states would destroy the validity of the well-established theory of mechanics. Furthermore, we show that non-negative definiteness of the density operator is not preserved in the negative direction in time which is in contradiction with the determinism principle.

Again, we start by describing the time evolution of the eigenvalues $\{p_i\}$ of the density operator. It is straightforward to show that Equation (5.8) yields

$$\frac{dp_i}{dt} = \langle \psi_i | \frac{\partial \rho}{\partial t} | \psi_i \rangle = \frac{1}{\lambda} \left(\langle \psi_i | \hat{\rho}(\rho) | \psi_i \rangle - p_i \right) = \frac{1}{\lambda} \left(\hat{\rho}_{ii} - p_i \right). \tag{C.15}$$

Because the density operator $\hat{\rho}(\rho)$ corresponds to a stable equilibrium state, is given by the canonical distribution. We consider a state ρ having a value of energy larger than the ground state energy of the system. Then the operator $\hat{\rho}(\rho)$ is positive definite. Therefore, if $p_i=0$, using Equation (C.15) we get

$$\frac{dp_i}{dt} = \frac{1}{\lambda}\hat{\rho}_{ii} > 0 . \tag{C.16}$$

But, this is exactly the same problem we had with the Lindblad equation, i.e., there exist mechanical states having an infinite rate of entropy generation

$$\frac{d\langle S \rangle}{dt} = -k\sum_i \frac{dp_i}{dt} \text{Log}(p_i) = +\infty \tag{C.17}$$

and the non-negativity of the density operator is preserved only in the positive direction in time. Therefore, we conclude that like the Lindblad equation, the Park-Simmons equation violates Conditions 5, 6, and 9 stated in Section 5.1, and is not acceptable.

C.3 The Beretta Equation

In this section, we provide the proof that the Beretta equation satisfies Conditions 7 and 8 established in Section 5.1. We also repeat the proofs that it also satisfies Conditions 1 to 6, originally given by Beretta [1984, 1985]. To simplify the notation, we consider a system in which the only generator of motion is the Hamiltonian, i.e., n=1 and the dissipative term in the Beretta equation is given by Equation (5.12b). The generalization of the results that follow is straightforward. We repeat the Beretta equation for a system for which the Hamiltonian is the only generator of motion:

$$\frac{\partial \rho}{\partial t} = \frac{1}{i\hbar}[H, \rho] + \frac{1}{2\tau}\{\rho, D(\rho)\}_+ \tag{C.18}$$

$$D(\rho) = \frac{\begin{vmatrix} \Sigma - \langle\Sigma\rangle & H - \langle H\rangle \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)}. \tag{C.19}$$

We begin by verifying that the Beretta equation satisfies Conditions 1 to 4. It is trivial to verify Condition 1. The trace of ρ is conserved because

$$\mathrm{Tr}\left(\frac{\partial \rho}{\partial t}\right) = \frac{1}{\tau}\mathrm{Tr}(\rho D(\rho)) = \frac{1}{\tau}\frac{\begin{vmatrix} \langle\Sigma\rangle - \langle\Sigma\rangle & \langle H\rangle - \langle H\rangle \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)} = \frac{1}{\tau}\frac{\begin{vmatrix} 0 & 0 \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)} = 0. \tag{C.20}$$

The value of the energy is conserved because

$$\mathrm{Tr}\left(H\frac{\partial \rho}{\partial t}\right) = \mathrm{Tr}(H\rho D(\rho)) = \frac{1}{\tau}\frac{\begin{vmatrix} (H, \Sigma) & (H, H) \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)} = 0 \tag{C.21}$$

i. e., the two rows of the determinant are identical. The value of entropy does not decrease in time because

$$\frac{d\langle S\rangle}{dt} = k\frac{d\langle\Sigma\rangle}{dt} = \frac{1}{\tau}\frac{\begin{vmatrix} (\Sigma, \Sigma) & (\Sigma, H) \\ (H, \Sigma) & (H, H) \end{vmatrix}}{(H, H)} \geq 0 \tag{C.22}$$

i. e., the Gram determinant in the numerator is nonnegative and, for any operator A, $(A, A) \geq 0$ due to the properties of semi-inner products [Conway, 1985].

First, we show that the beretta equation satisfies Condition 8, and then Condition 5. Beretta [1985a] showed that the solution of his equation exists and is unique for a two-level system. Here we present a general proof, which is not restricted by the dim(H).

The evolution of each eigenvalue p_i of the density operator obeys:

$$\frac{dp_i}{dt} = \left\langle \psi_i \left| \frac{\partial \rho}{\partial t} \right| \psi_i \right\rangle = \frac{1}{2\tau} \left\langle \psi_i \left| \{\rho, D(\rho)\}_+ \right| \psi_i \right\rangle = \frac{p_i}{\tau} \left\langle \psi_i \left| D(\rho) \right| \psi_i \right\rangle \qquad (C.23)$$

or, equivalently

$$\tau \frac{dp_i}{dt} = -p_i \text{Log}(p_i) + p_i \left(\frac{(H, \Sigma)}{(H, H)} (\langle H \rangle - H_{ii}) - \langle \Sigma \rangle \right) = -p_i \text{Log}(p_i) + C p_i \qquad (C.24)$$

where $H_{ii} = \langle \psi_i H \psi_i \rangle$. Because of the nonlinearity of Equation (C.24), the existence and the uniqueness of the solution must be proven. The first observation is that the logarithmic nonlinearity is harmless. For $p_i(0) > 0$, $p_i \text{Log}(p_i)$ is an analytic expression in a small neighborhood of $p_i(0)$, where $p_i(0)$ denotes the value of p_i at time t=0. Hence the existence and uniqueness of the solution is guaranteed for t>0 [Bender and Orszag, 1978]. For $p_i(0) = 0$, the logarithmic term causes no bifurcation, because it satisfies an Osgood condition [Ince, 1956]. This is also noted by Beretta [1984]. To show this point we rewrite the equation (C.24) in the form

$$\tau \frac{dp}{dt} = -p \text{Log}(p) + C p \qquad (C.25)$$

where we omit the index to simplify notation. If C were a constant, then dividing the equation by p, we would obtain a linear equation in u=Log(p) given by

$$\tau \frac{du}{dt} = -u + C \qquad (C.26)$$

which can be readily solved. The solution reads

$$u(t) = C\tau(\exp(-t/\tau)-1) + u(0)\exp(-t/\tau) \tag{C.27}$$

or, equivalently,

$$p(t) = p(0)\exp(\exp(-t/\tau))\exp\left[C\tau(\exp(-t/\tau)-1)\right] \tag{C.28}$$

This result shows that if $p(0)=0$, then $p(t)=0$ for all $t>0$. Because, this solution coincides with the trivial solution, the equation admits a unique solution for all values of $p(0) \geq 0$ despite the logarithmic singularity. This example simply illustrates the behavior of the Beretta equation. Equation (C.24) is not identical to Equation (C.25) however, because C is not a constant. Nevertheless, the existence and uniqueness of the solution is guaranteed if we can show that C is bounded, which is equivalent to saying that the second term on the right hand side of Equation (C.24) satisfies a Lipschitz condition [Bender and Orszag, 1978]. This is indeed the case.

Proof: Equation (C.21) shows that value of energy is conserved, hence <H> in Equation (C.24) is constant and finite throughout the time evolution. By virtue of the second law, for a given value of energy, amounts of constituents and parameters, there exists a state which has a largest value of entropy S_{max}. Infact, S_{max} is finite if <H> is finite (concavity of the stable equilibrium states curve on the S versus E plane, Fig. 3.1). Because, $<S>=k<\Sigma>$, $\Sigma_{max}=S_{max}/k$ and is finite. Therefore, $<\Sigma>$ is also bounded. The troublesome term is

$$\frac{(\Sigma, H)}{(H,H)}. \tag{C.29}$$

Using Cauchy-Schwarz inequality [Conway, 1985], we get

$$\frac{(\Sigma, H)}{(H, H)} \leq \frac{\sqrt{(H, H)}\sqrt{(\Sigma, \Sigma)}}{(H, H)} = \sqrt{\frac{(\Sigma, \Sigma)}{(H, H)}} .$$ (C.30)

However, $(\Sigma, \Sigma) = <\Sigma^2> - <\Sigma>^2$ is also bounded for given values of energy, amounts of constituents and parameters. The proof is similar to the proof that $<S>$ is bounded (we solved the maximization problem of entropy, given the constraints $Tr(\rho)=1$ and $Tr(H\rho)=$ fixed, in Appendix B). It is straightforward to show that $<\Sigma^2> = Tr(\rho(Log\rho)^2)$ is maximized when ρ is diagonal in the energy representation. Again, using Lagrange multipliers, we maximize the function $Tr(\rho(Log\rho)^2) - \lambda Tr(H\rho) - (\mu-1)Tr(\rho)$, and get

$$\left(Log(p_i)\right)^2 + 2Log(p_i) = \lambda \varepsilon_i + (\mu - 1)$$ (C.31)

where $\{\varepsilon_i\}$ are the energy eigenvalues. If we solve Equation (C.31) for $\{p_i\}$, we get

$$p_i = \frac{1}{e} \exp\left(-\sqrt{\lambda \varepsilon_i + \mu}\right) = \frac{\exp\left(-\sqrt{1 + \nu \varepsilon_i}\right)}{\sum_j \exp\left(-\sqrt{1 + \nu \varepsilon_j}\right)}$$ (C.32)

or, equivalently,

$$\rho_\nu = \frac{\exp\left(-\sqrt{I + \nu H}\right)}{Tr\left(\exp\left(-\sqrt{I + \nu H}\right)\right)}.$$ (C.33)

where $\nu = \lambda/\mu$, H and I are the Hamiltonian and identity operators, respectively. This result can be summarized as follows: the way the canonical distribution ρ_β maximizes $<S>$, ρ_ν maximizes $<\Sigma^2>$. Because both $<\Sigma^2>$ and $<\Sigma>$ are bounded, (Σ, Σ) is also

bounded. Although, there are a few mathematical technicalities that we justify later, this result shows that the term C in Equation (C.24) is bounded.

Because C is bounded, and the logarithmic term satisfies an Osgood condition, as we mentioned the solution of Equation (C.24) is unique for p(0)=0. For p(0)>0, the right hand side of Equation (C.24) satisfies a Lipschitz condition hence its solution exists and is unique. This proves that the Beretta equation admits a unique solution for every initial density operator, i.e., the Beretta equation satisfies Condition 8.

Among the technicalities we need to pay attention to in the proof, is that $<\Sigma^2>$ admits a maximum only if $\text{Tr}\left(\exp\left(-\sqrt{I+\nu H}\right)\right)<\infty$. This condition imposes a restriction on the Hamiltonian, similar to that established in Section 4.4. However, again for a system with finite volume, the WKB approximation guarantees that this condition is satisfied by the Hamiltonian. Another technicality is that we have to make sure that (H,H) does not vanish, otherwise the term in Equation (C.30) and hence C becomes unbounded. Note that $(H,H)=(\Delta H)^2=<H^2>-<H>^2$. It is easy to show that, (H,H) has a minimum when <H> does not correspond to an energy eigenvalue. Therefore, the only troublesome initial conditions can occur when <H> corresponds to an energy eigenvalue. For simplicity we assume that all the energy eigenvalues are non-degenerate, and show that (H,H) does not vanish. Assume that <H> corresponds to an energy eigenvalue ε_i, then (H,H) admits a minimum under the constraints <S>=fixed and Tr(ρ)=1. The problem is solved, again by using the method of Lagrange multipliers, and is found that (H,H) is minimum when the density operator has the form

$$\rho_\delta = \frac{\exp\left(-\delta(H-\langle H\rangle)^2\right)}{\text{Tr}\left(\exp\left(-\delta(H-\langle H\rangle)^2\right)\right)} \tag{C.34}$$

where δ>0. If initially the entropy <S>=0, then the system is initially in the energy eigenstate corresponding to eigenvalue ε_i=<H>. But then, (H,H)=0 initially, in which

case it is postulated that the equation of motion reduces to the von Neumann equation and the solution is unique (actually, this is an equilibrium state [Beretta, 1984]). However, if initially <S> is positive, we need to do some work to show that (H,H) does not come close to 0 throughout the time evolution. We project all the states with energy <H> onto the <S> versus (H,H) plane, which yields a graph (Figure C.1) identical to Figure 3.1. The state which has the minimum (H,H) for a given value of <S> correspond to a ρ_δ given by Equation (C.34). The curve representing such states is concave, and the proof of that fact is similar to the proof that the stable equilibrium states curve is concave on the S versus E plane (Section B.3). The key point is the concavity of the function $x\text{Log}(x)$, in the interval $0 \leq x \leq 1$. We denote by $(H,H)_{min}$ the smallest possible value of (H,H) that any state (with energy <H> and entropy $<S>_0$) can have, where $<S>_0$ is the initial value of entropy. By virtue of Equation (C.22), the value of entropy at any later instant of time t is larger than $<S>_0$. But, from Figure C.1, we immediately conclude that (H,H) at any later instant of time will be larger than $(H,H)_{min}$ which in turn is a non-zero number. Therefore, we have cleared the technicalities involved in the proof of the existence and uniqueness of the solutions of the Beretta equation.
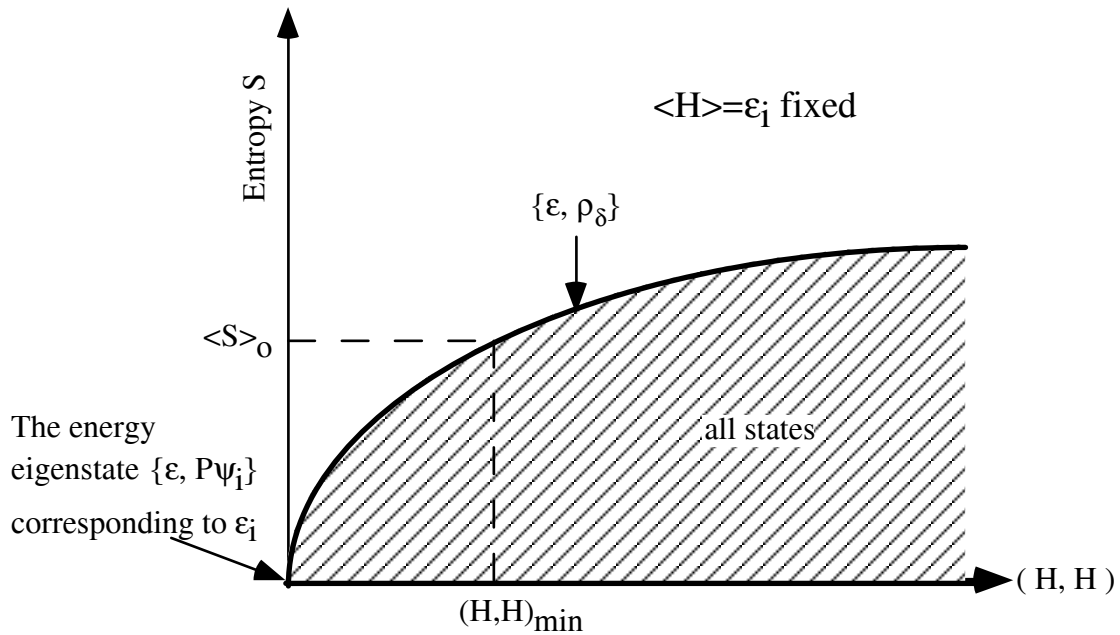
Figure C.1 Entropy versus (H,H) graph for a fixed value of $<H>=\epsilon_i$

It is also easy to show that the Beretta equation preserves the non-negative definiteness of the density operator, i.e., that it satisfies Condition 5. Because, in the unique solution of the Beretta equation, an eigenvalue which is initially zero always remains zero, no eigenvalue can cross the zero value and the non-negative definiteness of ρ is established.

Next, we show that the Beretta equation satisfies Condition 7. For simplicity, we choose two independent petit systems A and B, for which the only generators of motion are H_A and H_B, respectively. We solve the equation of motion for $\rho_A(t)$ for the initial condition $\rho_A(0)$. Similarly, we solve for $\rho_B(t)$ for the initial condition $\rho_B(0)$. The equation of motion for either system can be written as

$$\frac{\partial \rho_\alpha}{\partial t} = \frac{1}{i\hbar}[H_\alpha, \rho_\alpha] + \frac{1}{2\tau} \left\{ \rho_\alpha, \frac{\begin{vmatrix} \Sigma_\alpha - \langle \Sigma_\alpha \rangle & H_\alpha - \langle H_\alpha \rangle \\ (\Sigma_\alpha, H_\alpha) & (H_\alpha, H_\alpha) \end{vmatrix}}{(H_\alpha, H_\alpha)} \right\}_+ \tag{C.35}$$

where $\alpha = A, B$. Because, the two systems are independent the state at any instant of time t is $\rho_{AB}(t) = \rho_A(t) \otimes \rho_B(t)$. Taking the time derivative of this expression we get

$$\frac{\partial \rho_{AB}}{\partial t} = \frac{\partial \rho_A}{\partial t} \otimes \rho_B(t) + \rho_A(t) \otimes \frac{\partial \rho_B}{\partial t}. \tag{C.36}$$

Using the relations $H_{AB} = H_A \otimes I_B + I_A \otimes H_B$, $\Sigma_{AB} = \Sigma_A \otimes I_B + I_A \otimes \Sigma_B$, $\langle H_{AB} \rangle = \langle H_A \rangle + \langle H_B \rangle$, $\langle \Sigma_{AB} \rangle = \langle \Sigma_A \rangle + \langle \Sigma_B \rangle$, $(G_A \otimes I_B, I_A \otimes J_B) = 0$ for any operator G_A and J_B, and the well-known relations of determinants, we can show that the time evolution of the composite system obeys the Beretta equation

$$\frac{\partial \rho_{AB}}{\partial t} = \frac{1}{i\hbar}[H_{AB}, \rho_{AB}] + \frac{1}{2\tau}\{\rho_{AB}, D(\rho_{AB})\}_+ \tag{C.37}$$

where

$$D\left(\rho_{AB}\right) = \frac{\begin{vmatrix} \Sigma_{AB} - \langle\Sigma_{AB}\rangle & \tilde{H}_A - \langle\tilde{H}_A\rangle & \tilde{H}_B - \langle\tilde{H}_B\rangle \\ \left(\tilde{H}_A, \Sigma_{AB}\right) & \left(\tilde{H}_A, \tilde{H}_A\right) & \left(\tilde{H}_A, \tilde{H}_B\right) \\ \left(\tilde{H}_B, \Sigma_{AB}\right) & \left(\tilde{H}_B, \tilde{H}_A\right) & \left(\tilde{H}_B, \tilde{H}_B\right) \end{vmatrix}}{\begin{vmatrix} \left(\tilde{H}_A, \tilde{H}_A\right) & \left(\tilde{H}_A, \tilde{H}_B\right) \\ \left(\tilde{H}_B, \tilde{H}_A\right) & \left(\tilde{H}_B, \tilde{H}_B\right) \end{vmatrix}} \tag{C.38}$$

where $\tilde{H}_A = H_A \otimes I_B$ and $\tilde{H}_B = I_A \otimes H_B$. This result can be generalized to any system with arbitrary number of generators of motion. Furthermore, this is a beautiful example of a petit system A+B whose generator of motion is not the Hamiltonian H_{AB} alone. At first look, it seems that the Hamiltonian H_{AB} is not among the generators of motion, though this is not the case. By adding the second column of the determinant in the numerator to the third column, and by adding the first column of the determinant in the denominator to the second column, we see that the generators of motion can be expressed as $\{H_A, H_{AB}\}$. As we mentioned earlier, the linear independence of the generators of motion here plays the key role. Similarly, we can consider the generators of motion of the composite system as being either $\{H_{AB}, H_B\}$ or $\{H_A, H_B\}$.

This result can be generalized to systems with more than one generator of motion. If we denote by $\{G_{A,n}\}$ and $\{G_{B,m}\}$ the generators of motion of two independent systems A and B, respectively, it is straightforward to show that the generators of motion of the composite system A+B can be expressed as $\left\{\{\tilde{G}_{A,n}\} \cup \{\tilde{G}_{B,m}\}\right\}$, where $\tilde{G}_{A,n} = G_{A,n} \otimes I_B$ and $\tilde{G}_{B,m} = I_A \otimes G_{B,m}$. Accordingly, we conclude that the Beretta equation satisfies Condition 7.

Finally, we provide the proofs of Equations (5.24), (5.25) and (6.22). We consider a system A that admits two subsystems A_1 and A_2. The only generator of motion of system A is the Hamiltonian operator H, and therefore the Beretta equation is

given by Equations (C.18) and (C.19). We assume that the density operator of the system at time t=0 is given by

$$\rho(0) = \rho_1(0) \otimes \rho_2(0) \tag{C.39}$$

where the density operators of the two subsystems are given by the canonical distributions

$$\rho_i(0) = \frac{\exp(-\beta_i H_i)}{\text{Tr}(\exp(-\beta_i H_i))} \quad \beta_i = \frac{1}{kT_i} \quad i = 1,2 \tag{C.40}$$

and T_1 and T_2 are the temperatures of subsystems A_1 and A_2, respectively. We denote the eigenvectors of H_1 and H_2, by $\{\psi_i\}$ and $\{\phi_j\}$, respectively, i.e.,

$$H_1\psi_i = e_i\psi_i \quad \text{and} \quad H_2\phi_j = \varepsilon_j\phi_j. \tag{C.41}$$

Accordingly, the eigenvectors of the Hamiltonian operator are $\{\psi_i \, \phi_j\}$, i.e.,

$$H(\psi_i \otimes \phi_j) = (e_i + \varepsilon_j)(\psi_i \otimes \phi_j). \tag{C.42}$$

At time t=0, the density operator of the system is given by the canonical distribution, hence we have the relations

$$\rho_1(0)\psi_i = p_i(0)\psi_i \quad , \quad \rho_2(0)\phi_j = q_j(0)\phi_j. \tag{C.43}$$

$$\rho(0)(\psi_i \otimes \phi_j) = p_i(0)q_j(0)(\psi_i \otimes \phi_j) = p_{ij}(0)(\psi_i \otimes \phi_j) \tag{C.44}$$

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Because the density operator at time t=0 is diagonal in the energy representation, it follows from Equation (C.19) that $D(\rho)$ is diagonal in the energy representation, and from Equation (C.18) that $\dfrac{\partial \rho}{\partial t}$ is diagonal in the energy representation. Therefore, we conclude that at any instant of time t, the density operator of the system remains diagonal in the energy representation. This is equivalent to saying that the eigenvectors of the density operator are $\{\psi_i \otimes \phi_j\}$ at any instant of time t, and the density operator satisfies the eigenvalue problem given by

$$\rho(t)\left(\psi_i \otimes \phi_j\right) = p_{ij}(t)\left(\psi_i \otimes \phi_j\right). \tag{C.45}$$

It remains to show that the eigenvalues of the density operator evolve such that

$$\rho(t) = \rho_1(t) \otimes \rho_2(t) \tag{C.46}$$

$$\text{where } \rho_i(t) = \frac{\exp(-\beta_i H_i)}{\text{Tr}\left(\exp(-\beta_i H_i)\right)} \quad \beta_i = \frac{1}{kT_i} \quad i = 1,2 \tag{C.47}$$

with time dependent temperatures T_1 and T_2 of subsystems A_1 and A_2, respectively. It is straightforward to verify that each of the eigenvalues $\{p_{ij}\}$ of the density operator satisfies the relation

$$\frac{dp_{ij}}{dt} = \left\langle \left(\psi_i \otimes \phi_j\right) \left| \frac{\partial \rho}{\partial t} \right| \left(\psi_i \otimes \phi_j\right) \right\rangle. \tag{C.48}$$

Using the Beretta equation Equations (C.18) in Equation (C.48), we obtain the relation

$$\tau \frac{dp_{ij}}{dt} = -p_{ij} \text{Log}\left(p_{ij}\right) - \langle \Sigma \rangle p_{ij} - \frac{(H, \Sigma)}{(H, H)}\left(e_i + \varepsilon_j\right)p_{ij} + \frac{(H, \Sigma)}{(H, H)} \langle H \rangle p_{ij} \tag{C.49}$$

for all pair of indices {i,j}.

If the solution is indeed of the form given by Equations (C.46) and (C.47), at any instant of time t, the eigenvalues $\{p_{ij}\}$ of the density operator must satisfy the relations given by

$$\text{Log}\left(\frac{p_{ij}}{p_{kl}}\right) = -\beta_1(t)(e_i - e_k) - \beta_2(t)(\varepsilon_j - \varepsilon_l) \tag{C.50}$$

for all pairs of indices {i,j} and {k,l}. If the existence of $\beta_1(t)$ and $\beta_2(t)$ such that Equations (C.50) are simultaneously satisfied for all pairs of indices {i,j} and {k,l} at all instants of time can be established, then the uniqueness of the solution of the Beretta equation guarantees that the density operator is given by Equations (C.46) and (C.47). Because these relations are satisfied at t=0, all we need to show is that the derivative of each relation with respect to time is satisfied. Taking the time derivative of Equation (C.50), we find

$$\frac{d}{dt}\text{Log}\left(\frac{p_{ij}}{p_{kl}}\right) = -\frac{d\beta_1}{dt}(e_i - e_k) - \frac{d\beta_2}{dt}(\varepsilon_j - \varepsilon_l). \tag{C.51}$$

for all pairs of indices {i,j} and {k,l}. The logarithmic derivative on the left hand side of each of Equations (C.51) can be evaluated directly from Equations (C.49), and is equal to

$$\frac{d}{dt}\text{Log}\left(\frac{p_{ij}}{p_{kl}}\right) = \frac{1}{\tau}\left(\beta_1 - \frac{(H,\Sigma)}{(H,H)}\right)(e_i - e_k) + \frac{1}{\tau}\left(\beta_1 - \frac{(H,\Sigma)}{(H,H)}\right)(\varepsilon_j - \varepsilon_l). \tag{C.52}$$

Comparison of Equations (C.52) and (C.51) reveals that, there exist $\beta_1(t)$ and $\beta_2(t)$ satisfying the relations

$$
\begin{cases}
\dfrac{d\beta_1}{dt} = -\dfrac{1}{\tau}\left(\beta_1 - \dfrac{(H,\Sigma)}{(H,H)}\right) \\[3mm]
\dfrac{d\beta_2}{dt} = -\dfrac{1}{\tau}\left(\beta_2 - \dfrac{(H,\Sigma)}{(H,H)}\right)
\end{cases}
\tag{C.53}
$$

such that Equations (C.51) can indeed be simultaneously satisfied for all pairs of indices $\{i,j\}$ and $\{k,l\}$. Hence the relations given by Equations (C.51) are simultaneously satisfied for all pairs of indices $\{i,j\}$ and $\{k,l\}$ at all instants of time. Accordingly, we conclude that the solution of the Beretta equation has the form given by Equations (C.46) and (C.47). Furthermore, it follows directly from Equation (C.53) that we have

$$
\frac{d}{dt}(\beta_1 - \beta_2) = -\frac{1}{\tau}(\beta_1 - \beta_2).
\tag{C.54}
$$

which is Equation (5.25) given in Chapter 5.

The proof of the validity of Equation (6.22) is a straightforward generalization of the proof we have just presented. It is essential to recognize that the number of constituent operator N commutes with the Hamiltonian operator H. Therefore, Equations (C.50) and (C.52) are modified such that they not only contain energy eigenvalues $\{e_{ij}\}$ but also the number of constituent eigenvalues $\{n_{ij}\}$.

C.4 About the Zero Eigenvalues of ρ

At the end of Chapter 4, we claim that any equation of motion which does not preserve the zero eigenvalues of ρ, violates at least one of Conditions 5, 6, 8, or 9 stated in Section 5.1. Indeed, from the assumed form of the equation of motion of quantum thermodynamics (Equation (5.1)), it is clear that the change in an eigenvalue p_i of ρ can be expressed as

$$\frac{dp_i}{dt} = f(p_1, \ldots, p_i, \ldots). \tag{C.55}$$

Consider that initially, $p_i=0$ for $i \geq 2$, and $f(p_1, \ldots, 0, \ldots) > 0$, which is exactly the same situation encountered with either the Lindblad equation or the Park-Simmons equation. Then, the rate of entropy generation in a pure state would be infinite (Equation (C.14)). If this is the case, however, the equation of motion does not reduce to the von Neumann equation, even as an approximation, i.e., violates Condition 6. Furthermore, the existence of pure state which are extremely dissipative and unstable is also contradictory to our experimental observations. Accordingly, the equation of motion violates Condition 9. Moreover, the eigenvalue p_i of the density operator becomes negative for negative values of time. Therefore, the non-negative definiteness of the density operator is not preserved in the negative direction in time, and the equation of motion does not comply with the determinism principle (Condition 5).

On the other hand, if initially $p_i=0$ for $i \geq 2$, and $f(p_1, \ldots, 0, \ldots)=0$, then a solution of Equation (C.55) is $p_i(t)=0$ for $t \geq 0$, in which case the zero eigenvalue is preserved. Yet, due to nonlinearity of the function $f(p_1, \ldots, p_i, \ldots)$ we can have another solution $p_i(t) \neq 0$ for $t>0$. But then, the equation of motion does not admit a unique solution, i.e., violates Condition 8.

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