Intrinsic Quantum Thermodynamics: Application to Hydrogen Storage on a Carbon Nanotube and Theoretical Consideration of Non-Work Interactions

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Abstract

Intrinsic Quantum Thermodynamics (IQT) is a theory that combines Thermodynamics and Quantum Mechanics into a single theory and asserts that irreversibility and the increase of entropy has its origin at the fundamental, atomistic level. The merits and details of IQT are discussed and compared with the well-known theory of Quantum Statistical Mechanics (QSM) and the more recent development of Quantum Thermodynamics (QT). IQT is then used to model in 3D the time evolution of the adsorption of hydrogen on a single-walled carbon nanotube. The initial state of the hydrogen molecules is far from stable equilibrium and over time the system relaxes to a state of stable equilibrium with the hydrogen near the walls of the nanotube. The details of the model are presented, which include the construction of the energy eigenlevels for the system, the treatment of the interactions between the hydrogen and the nanotube along with the interactions of the hydrogen molecules with each other, and the solution of the IQT equation of motion as well as approximation methods that are developed to deal with extremely large numbers of energy eigenlevels. In addition, a new extension to the theory of IQT is proposed for modeling systems that undergo heat interactions with a heat reservoir. The formulation of a new heat interaction operator is discussed, implemented, tested, and compared with a previous version extant in the literature. IQT theory is then further extended to encompass simple mass interactions with a mass reservoir. The formulation, implementation, and testing of the mass interaction operator is also discussed in detail. Finally, IQT is used to model the results of two experiments found in the literature. The first experiment deals with the spin relaxation of rubidium atoms and the second examines the relaxation behavior of a single trapped ion that is allowed to interact with an external heat reservoir. Good agreement between experiment and the model predictions is found.
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It has been my goal and passion to do interesting and cutting edge research in a field of interest, specifically non-equilibrium thermodynamics, and to hopefully apply this knowledge to understanding the larger physical world. Over the last few years I have had a special opportunity to follow this type of research at Virginia Tech in the study of Intrinsic Quantum Thermodynamics under Dr. Michael R. von Spakovsky. For this opportunity I am exceedingly grateful. I would like to give my thanks and express my sincere gratitude to my advisor Dr. von Spakovsky for providing his guidance and kind support in this work. His example and the collaborations that I have had with him have been invaluable and have given me courage to pursue truth even in the face of daunting obstacles. I have learned and grown from the challenges that I have faced with the help of him and other of my colleagues.

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Chapter 1 - Introduction and Background

1.1 Introduction

The foundations of the theory of Intrinsic Quantum Thermodynamics (IQT) were first developed beginning in 1976 by Hatsopoulos and Gyftopoulos (Hatsopoulos and Gyftopoulos, 1976a,b,c,d) with an important fundamental contribution a few years thereafter by Beretta (Beretta, 1981). The theory of IQT is based on the assertion that the Second Law of Thermodynamics applies at all levels of description including the atomistic, which contrasts with the view in traditional Quantum Mechanics (QM) that suggests that the Second Law at the microscopic level plays no role since it is purely phenomenological in nature.

QM sees nature in terms of its most basic physical processes as being reversible and as only involving the fundamental properties of inertial mass, momentum, and energy but not of entropy. To get at the concept of entropy from such a standpoint has traditionally been done by the inclusion of an additional description, namely, that of Statistical Mechanics (SM). The result, Quantum Statistical Mechanics (QSM), provides a basis for the entropy as well as for the entropy generation that is said to result from the irreversible processes observed at a phenomenological level of description and perhaps even at a fundamental level of description. A more recent approach called Quantum Thermodynamics (QT – originally dissipative QM) QT has extended traditional QM through the use of a so-called “open system” (ie., closed system plus reservoir) model to the realm of Non-equilibrium Thermodynamics (NET) via the assumption that the dissipative nature of a system is due to the build-up and loss (ie, “dissipation”) of a set of extrinsic correlations resulting from weak interactions between the closed system and reservoir (Gemmer, Michel and Mahler, 2004, 2009; Zurek, 1991; Zurek, 1993; Zurek and Paz, 1994). Supporting experimental evidence over the last 35 years has included such phenomena as quantum decoherence, entanglement, tunneling, etc. (Beretta, 2008; Kleinekathöfer, 2009; Blum 1996; Coffey et al. 2007; Yu et al. 2000; Nakatani and Ogawa, 2007; Pomyalov and Tanner, 2005).
Unfortunately, as with the Classical Statistical Mechanical (CSM) description, which leads to the Boltzmann equation of motion (an irreversible equation derived from the reversible Liouville-Hamiltonian description), the basis for the entropy and the entropy generation originates from a set of either exogenous statistics or extrinsic correlations. The result is a paradox, i.e., the so-called Loschmidt paradox (Loschmidt, 1876; Beretta, 2009b). Consequently, the conclusion is reached that entropy and entropy generation are illusions without physical foundation. Countering this view is that of IQT which ejects SM from the description and like QT extends QM to the thermodynamic realm, but unlike QT does so without the open system model. IQT assumes that the Second Law at a fundamental level of description is due to the endogenous (intrinsic) quantum mechanical measurement statistics of the closed isolated system alone. The result is a unification of QM and Thermodynamics and a physical basis for the entropy and entropy generation.

Figure 1.1. Depiction of an energy versus entropy ($E$-$S$) diagram for the domains of equilibrium and non-equilibrium thermodynamics as well as quantum/classical mechanics. (von Spakovsky 2008; Beretta 2009a,b).

1.2 Quantum Mechanics and Equilibrium Thermodynamics

The theories of QM and Equilibrium Thermodynamics (ET) were developed independently and have enjoyed great success. The first theory governs the world of the microscopic, the almost unimaginably tiny, where particles have wave-like properties. The energy and matter of a system are not a continuum but are broken up into discrete pieces. What
is thought of as solid matter can interact in unexpected ways, for example, resulting in the creation of interference patterns similar to what is seen for waves at macroscopic scales. The second theory deals with the macroscopic world and with such concepts as heat, work, and temperature where quantum effects are often so subtle they are justifiably ignored.

Direct connections between the two theories, however, are not entirely lacking. In most texts on statistical mechanics, quantum mechanical arguments and the maximum entropy principle (or minimum energy principle) are used to derive quantum representations, using canonical and grand canonical distributions and partition functions of the properties, which characterize the stable equilibrium states of ET (e.g., Chandler 1987; Tien and Lienhard, 1979). These states are depicted for a system with constant parameters (e.g., \( \bar{\beta} = \{V\} \) where \( V \) is the volume) and constant composition \( \{n_1, ..., n_r\} \) in Figure 1.1, which shows the curve of all stable equilibrium states in the energy-entropy (\( E-S \)) plane. The temperature of the system, a strictly stable equilibrium concept, is represented by the slope of this curve at any given energy. There are no physically valid thermodynamic states to the right of or below this curve. The vertical axis at zero entropy represents the regime governed by QM and its equation of motion, the Schrödinger equation\(^1\). Between the vertical axis and the curve of stable equilibrium states is a region of not stable equilibrium states, i.e., non-equilibrium, steady, unsteady, and metastable and unstable equilibrium states. An isolated system in a non-equilibrium state within this region spontaneously moves to the right along a trajectory of successive states of higher entropy until stable equilibrium is reached.

The question which naturally arises, is if QM and ET represent the boundaries of the region of not stable thermodynamic states as shown in Figure 1.1 should it not in principle be possible to use quantum arguments at a fundamental level of description to describe the dynamics of the region of not stable equilibrium states as well? The problem however, is that the equation of motion of QM, the time-dependent Schrödinger equation, lacks the Second Law and as a consequence cannot describe the irreversible relaxation to stable equilibrium which occurs in this region.

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\(^1\) Of course, classically, the vertical axis represents states in Newtonian mechanics and its equation of motion is that derived from Newton’s Second Law.
1.3 The Equation of Motion of QM

The Schrödinger equation is given by

\[ i\hbar \frac{\partial}{\partial t} \Psi = H \Psi \]  

(1.1)

and describes the time evolution of state of a system in going from one pure state to another. All system states remain on the vertical (energy) axis of Figure 1.1. In this equation, \( |\Psi(\vec{x},t)\rangle \) is the state vector\(^2\) and is said to contain that information at any given instant of time that characterizes the state of the system. The operator \( H \) is the Hamiltonian operator expressed as

\[ H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) \]  

(1.2)

with \( \hbar = h/2\pi \) where \( h \) is Planck’s constant. The first term on the right hand side of the equation represents the kinetic energy of the system while \( V \) is the potential energy term. Using separation of variables with

\[ |\Psi(\vec{x},t)\rangle = \langle \Psi(t)|u(\vec{x})\rangle \]  

(1.3)

the time-independent and time-dependent parts of the Schrödinger equation are obtained. The former, the so-called energy eigenvalue equation, is written as

\[ H|u(\vec{x})\rangle = E|u(\vec{x})\rangle \]  

(1.4)

where \( E \) is an energy eigenvalue equivalent to the value which would be obtained upon measurement of the energy of the system and \( |u(\vec{x})\rangle \) its corresponding eigenvector. Solving this equation establishes the set of energy eigenlevels which characterize the system’s energy structure. The energy eigenvalues are then used in the time-dependent Schrödinger equation given by

\[ \frac{d|\Psi(t)\rangle}{dt} = -\frac{i}{\hbar} H|\Psi(t)\rangle \]  

(1.5)

to determine the change in state of the system. The changes of state are strictly unitary processes, i.e., a special class of reversible processes which take the system from one pure state to another.

\(^2\) The set of state vectors (vectors of norm 1) of a Hilbert space corresponds one-to-one with a set of wave functions (Merzbacher, 1998).
It is possible to transform equation (1.5) into operator format by first recognizing that the state vector can be expressed as an operator via a projector, i.e.,

\[ \rho(t) = |\psi(t)\rangle\langle\psi(t)| \]  

(1.6)

Then taking the time derivative of this density (or state) operator and substituting into equation (1.5) yields (e.g. Blum, 1996),

\[ \frac{d\rho}{dt} = \frac{d}{dt}(\langle\psi| + |\psi\rangle)\frac{d\langle\psi|}{dt} = -\frac{i}{\hbar}H|\psi\rangle\langle\psi| + |\psi\rangle\langle\psi|i\hbar H \]  

(1.7)

Using equation (1.6), this reduces to the von Neumann equation

\[ \frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] \]  

(1.8)

where the brackets are Poisson brackets. The term to the right of the equals is zero when \( \rho \) and \( H \), which are Hermitian operators, commute.

Equations (1.5) and (1.8) are expressions of the dynamical postulate of QM. The dynamics are strictly linear and describe a reversible unitary process such that the time evolution of the density operator \( \rho \) is expressed as (e.g., Hatsopoulos and Gyftopoulos, 1976),

\[ \rho(t_2) = T(t_2, t_1)\rho(t_1)T^+(t_2, t_1) \]  

(1.9)

The quantities \( t_1 \) and \( t_2 \) are initial and final times, respectively, \( T(t_2, t_1) \) is a unitary time evolution operator, and \( T^+(t_2, t_1) \) its Hermitian conjugate. When \( H \) for the system does not change in time, i.e., when the values of the system parameters \( \vec{\beta} \) are fixed, then \( T(t, t_1) \) is given by

\[ T(t, t_1) = \exp[-(2\pi i/\hbar)H(t-t_1)] \]  

(1.10)

If instead the Hamiltonian \( H(t) \) is an explicit function of time, \( T(t, t_1) \) is expressed as

\[ T(t, t_1) = -\int_{t_1}^{t} (2\pi i/\hbar)H(t)T(t, t-1)dt \]  

(1.11)

The above dynamic postulate, because it is based on unitary transformations and linear dynamics, cannot be used as a basis for describing irreversible processes, which require a non-linear dynamics. In addition, reversible processes whose end points are not related by a unitary operator are also not covered (e.g., the transfer of energy in a reversible heat interaction from a high to a low temperature). Hence, the time-dependent Schrodinger and von Neumann equations describe how the state of a system evolves in time only when the entropy for the system is zero and unvarying. The time evolution does affect the likelihood (e.g., Messiah, 1976; Shankar,
1994) of finding the particles of a system in a given region of the system, but it does not change the amount of energy within the system that is available for doing work i.e., the adiabatic availability (Gyftopoulos and Beretta, 2005). To do so would require a change in system entropy \( \langle S \rangle \), as determined by

\[
\langle S \rangle = -k_b \text{Tr}(\rho \ln \rho)
\]  

with corresponding changes over time to the eigenvalues of \( \rho \) the state operator. However, this is impossible with the linear dynamics of the von Neumann equation and equivalently of the Schrödinger equation.

### 1.4 The Irreversibility Paradox

Conflicts naturally arise between QM and ET with regard to such notions as reversibility, the adiabatic availability of energy, and the existence of stable equilibrium states. QM is linear and based on a fundamental description which concerns itself with individual particles while ET is phenomenological. Incompatibilities result from a difference in the general features of each theory’s kinematics and dynamics\(^3\). In an attempt to bridge the gap between QM and ET, SM is used. However, even with this bridging, the incompatibilities are still left intact. Nonetheless, the statistical approach has led to many successes that include the stable equilibrium expressions found from Statistical Thermodynamics (ST) (Tien and Lienhard, 1979, Hill, 1987), Density Functional Theory (DFT) (Parr and Yang, 1989), and Quantum Chemistry (Schatz and Ratner, 1993; Hampel and Werner, 1996; Schutz, 2002; Crawford, 2006; Russ and Crawford, 2004). Other applications include the theoretical extensions to non-equilibrium thermodynamics such as the Boltzmann equation and master equations (e.g., Fokker-Planck, BGK, etc.) of CSM (Harris, 1971), (Liboff, 1979), the Onsager reciprocity relations, the Callen fluctuation-dissipation relations, and the master equations of Quantum Dissipative Dynamics, which recently has been renamed as Quantum Thermodynamics (Beretta, 2009; Kossakowski, 1972a,b,c; Ingarden and Kossakowski, 1975; Lindblad, 1976; Gemmer, Michel and Mahler, 2004, 2009; Zurek, 1991; Zurek, 1993; Zurek and Paz, 1994).

These theories have been successful in regularizing experimental evidence. However, this is insufficient if the predictions are incomplete. Their principles of dynamics must be

\(^3\) The kinematics describes the results of the motion, e.g., the state of a system, while the dynamics describes the motion itself.
complemented with some additional reasonable principle in order to be able to derive non-equilibrium expressions such as the Onsager relations or the Callen fluctuation-dissipation relations, or explain such phenomena as quantum entanglement and decoherences. The supplemental assumptions include microscopic reversibility, or small perturbations to ensure linear behavior, the existence of correlations between the system and reservoir which cyclically build up and disappear, or approximations (e.g., sufficiently small deviations from stable equilibrium). Thus, any approach based on SM or QT cannot lead to a general description of non-equilibrium. This is what is often called the “irreversibility paradox”, the resolution of which requires simultaneously addressing the following issues:

i. What the physical roots of “entropy” and “irreversibility” are;

ii. Whether or not “entropy generation” due to irreversibility is merely “a kind of statistical illusion”; 

iii. What a general description of non-equilibrium is.

The existing SM and QT paradigms are unable to resolve these issues for a number of straightforward reasons.

The first stems from the lack of a consistent definition for the entropy of Thermodynamics. Gyftopoulos and Çubukçu (1997) evaluate the most prevalent expressions for the entropy of thermodynamics found in the ET, CSM, QSM, and IQT literature, each with their own particular characteristics. Excluded are expressions for entropy based on temperature and heat since these are restricted to stable equilibrium. Expressions from CSM are eliminated since these are based on statistical (subjective) rather than quantal (inherent) probabilities. Finally expressions from QSM which depend on variables other than the eigenvalues of the state operator \( \rho \) are not acceptable since these fail to maintain the entropy invariant during a unitary process. The authors then define a clear rationale of eight criteria for choosing a quantal expression for entropy. The heart of their argument is based on the idea that entropy is related to the amount of internal energy that can be extracted adiabatically in a work interaction from the system, given that the state operator \( \rho \) is defined as it is in IQT. Only the expression for \( \langle S \rangle \) given by equation (1.2) satisfies all eight criteria.

A second reason for the failure of the statistical paradigm, in particular QSM, is that the concept of “state of a system”, a bedrock of physical thought, is lost since the “state of the
“ensemble” of the set of identical systems used to define the state operator $\rho$ no longer coincides with the state of the system (Park, 1968; Park and Simmons 1983). The state of the ensemble is a statistical collection of different states each with their own statistical mechanical probability. Such an ensemble is said to be heterogeneous, i.e., one in which the states of the identical systems are not all identically prepared (Hatsopoulos and Gyftopoulos, 1976). A consequence of defining the state operator in this way is that in a state of stable equilibrium, the entire ensemble has zero adiabatic availability so that no energy in a work interaction (with set of parameters $\beta$ and amounts of constituents $\vec{n}$ fixed, see Figure 1.1) can be extracted while the parts making up the ensemble necessarily have an adiabatic availability greater than zero and the possibility for doing work (Hatsopoulos and Gyftopoulos, 1976). Heterogeneous ensembles therefore allow for violations of the second law of thermodynamics (Hatsopoulos and Gyftopoulos, 1976). In contrast, the state operator $\rho$ of IQT results in no such violation. Furthermore, the notion of the “state of the system” is preserved by basing $\rho$ on a homogeneous ensemble consisting of identical systems that are identically prepared i.e., in the same state (Hatsopoulos and Gyftopoulos, 1976). As a result the adiabatic availabilities of the sub-ensembles must equal that of the ensemble.

Another reason for the failure of the statistical paradigm to address the irreversibility paradox is as has already been discussed that since the governing equation of QM is reversible, there is a categorical exclusion of the possibility of an irreversible evolution of state for any system. Yet we see and are acquainted with what look like irreversible processes every day. Nevertheless, if our most fundamental physical description of the universe, QM, is reversible, the entropy really does not exist despite what observation tells us. Or does it? Is perhaps the problem really that QM is correct but incomplete (Hatsopoulos and Gyftopoulos, 1976)?

1.5 Principal Approaches for Resolving the Irreversibility Paradox

Several approaches have been put forward to try to address the Irreversibility Paradox. The School of Prigogine acknowledges that entropy is likely to be a microscopic phenomenon and emphasizes the role of instability and bifurcations (e.g., the theory of dissipative structures) and the use of superlinear operators to modify the von Neumann equation (Wehrl, 1978; Park and Simmons, 1983). Simmons and Park (1981), however, conclude this approach cannot be general nor does there appear to be any actual phenomena that this theory has explained.
A second approach is the development and use of nonlinear Schrödinger equations (NLSE). Non-dissipative forms of the NLSE have been applied to quantum systems such as quantum condensates (Ruprecht, Holland and Burnett, 1995; Bronski et al. 2001) and nonlinear optics (Agrawal, 2000) but are also used for macroscopic phenomena such as in hydrodynamics (Zakharov, 1968), nonlinear acoustics (Crighton, 1979) and heat pulses in solids (Taha and Ablowitz, 1984). Dissipative versions of the NSLE, (e.g., Schuch, 2010; Goldin, 2000, 1996; Doebner and Goldin, 1992) attempt to model irreversible effects by including a frictional term directly in the Schrödinger equation. There is no use of the statistics of SM and the resulting dynamics are non-unitary so there is no a priori conflict with the irreversibility paradox. There have been other problems, however. Since the equation is nonlinear, the sum of two solutions may itself not be a solution to the NLSE, thereby violating the superposition principle. Furthermore, energy may not be conserved. As Çubukçu (1993) points out, the resulting density operators are not unique which may lead to more than one von Neumann equation that describes the same system evolution. Moreover, the source of the dissipation is phenomenological, usually viscous in nature, and not fundamental.

Another approach, that of QT, is based on the development and use of Markovian and non-Markovian quantum master equations (QMEs) for so-called “dissipative open systems” (Gemmer, Michel and Mahler, 2004, 2009; Zurek, 1991; Zurek, 1993; Zurek and Paz, 1994). Applications of these QMEs have been somewhat limited, e.g., to optics, quantum electronic devices, Brownian motion of single particles, absorption and emission spectra, and molecular wires (Kleinekathöfer, 2009; Blum, 1996; Coffey et al. 2007, Yu et al. 2000; Nakatani and Ogawa, 2007). Furthermore, the dissipative description of these “open systems” relies on a closed-system-plus-reservoir model. The time evolution of state is governed by the standard Schrödinger and von Neumann equations, while that for the closed system alone is governed by a QME derived from these equations (e.g., the well-known Kossakowski-Sudarshan-Gorini-Lindblad (KSGL) equation (Liboff, 1979; Kossakowski, 1972; Ingarden and Kossakowski, 1975; Lindblad, 1976) or its equivalents. The overall linear dynamics (i.e., that of the closed-system-plus-reservoir) is, thus, reversible and unitary yet gives rise to a closed-system linear dynamics which is irreversible and non-unitary. Irreversible relaxation to stable equilibrium is, thus,

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4 By “closed system” here the thermodynamic meaning, which is a system without mass interactions that may or may not be isolated with respect to heat and work interactions, is used.
accomplished at the expense of introducing the Loschmidt paradox (Kossakowski, 1972). In fact, common to all attempts at justifying the validity of these relaxations via QMEs is that they require additional, question-begging assumptions, e.g., that the build-up and erasure of correlations between the closed system and reservoir are sufficiently rapid to effectively maintain the system and reservoir decorrelated at all times (Beretta, 2009a).

In addition, an inherent conflict exists within QT with regard to the Second Law. Since reversible dynamics govern the system plus reservoir as a whole, the adiabatic availability, i.e., the ability of the system plus reservoir to do work, does not change as the system relaxes to mutual stable equilibrium with the reservoir. The implication then from QT is that it is possible to extract work directly from the internal energy of a system (or reservoir) at stable equilibrium without the need for gradients between the system and reservoir, i.e., a perpetual motion machine of the second kind can be constructed.

In contrast to all of these approaches, IQT and its equation of motion, the Beretta equation (Beretta, 2009a,b; Beretta, Gyftopoulos and Park, 1985; Beretta, 1986, Beretta, 2006a,b; Beretta, 2005; Beretta 2007; Gheorghiu-Svirschevski, 2001; Beretta, 2008; Beretta, 2010; Beretta, 2001; Beretta et al., 1984) circumvent the difficulties encountered in these other approaches. In particular, the Loschmidt paradox of QSM and QT is avoided since the dissipations of the closed system minus the reservoir are assumed to be strictly internal to the system and are fully captured by the nonlinear dynamics of the Beretta equation. IQT, thus, is able to determine the unique non-equilibrium path, which the system takes and which once known, allows one to determine, for example, the non-equilibrium thermodynamic properties (e.g., the chemical potentials and affinities) of each species, the kinetics of any reactions present, and the entropy generated due to irreversibilities at each instant of time. The latter, in fact, represents the dissipation or destruction of the non-conserved system property, the adiabatic availability (Gyftopoulos and Beretta, 2005). Furthermore, the path found is unique and fixed in an absolute sense at least to the extent that the relaxation times of QT are tied directly to experimental values and the time-energy Heisenberg uncertainty principle (Beretta, 2010).

Another contrast is that IQT emphasizes stability, i.e., that the essence of the Second Law of Thermodynamics is the existence and uniqueness of globally stable equilibrium states. Furthermore, the principal characteristics of IQT are that it
• is a single theory whose kinematics and dynamics encompass those of QM, which is a special case;
• requires no statistical, phenomenological or information-theoretic analogies as used with the QSM approach;
• applies to all systems large or small in any state (stable equilibrium and not stable equilibrium);
• places the Second Law in the hierarchy of physical laws on the level of those of QM;
• defines the entropy as an intrinsic property of matter that is a measure of the degree of energy load sharing between available system energy eigenlevels;
• defines the entropy generation as a manifestation of the spontaneous internal energy redistribution of the energy load;
• captures the linear and non-linear dynamics of this redistribution via the Beretta equation of motion.

It should be evident that among the features listed for the IQT paradigm, there is a very straightforward explanation for the physical origin of the entropy that is compatible with both QM and ET. Entropy is simply the tendency of the energy of a system to distribute itself amongst the available degrees of freedom, i.e., among all the available system energy eigenlevels. In a state of non-equilibrium, this distribution continues until no further change is possible, i.e., until a final state of maximum entropy and stable equilibrium have been reached. Since the entropy of an isolated system never decreases, the change in entropy and of state is irreversible. There is no need for the statistics of SM that count the number of configurations of so-called micro-states that make up a system’s macro-state. There is no need to worry about what information about the system may be missing such as correlations between system and reservoir, a mechanism that in fact does not lead to an increase in entropy.

1.6 Intrinsic Quantum Thermodynamics: The Basic Postulates and the IQT Equation of Motion

The IQT formalism is based on four non-dynamical postulates – i.e., systems, correspondence, state preparations, and observables-measurements-data-ensembles postulates – and a single dynamical postulate, the Beretta equation of motion. The first four postulates are the fundamental postulates of quantum mechanics that have in some ways been more rigorously
defined, for instance, in the way a state can be prepared. The fifth postulate governs how systems evolve thermodynamically with time. Contained therein as a special case, is the dynamical postulate of QM. Also implicit in the equation of motion of IQT are the First and Second laws of Thermodynamics and, as a consequence, the existence of unique, stable equilibrium states. Each of the five postulates is briefly described below (Beretta, 1984; Hatsopoulos and Gyftopoulos, 1976).

The first postulate of IQT, the systems postulate, describes the idea of a physical system and its correspondence with the properties of the space in which it is embedded. Thus, to every physical system there corresponds a complex, separable, complete inner product space, i.e., a Hilbert space $\mathcal{H}$. The Hilbert space of a composite system of two distinguishable subsystems 1 and 2 with the associated Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$, respectively, is the direct product space $\mathcal{H}_1 \otimes \mathcal{H}_2$. Note that the concept of distinguishability implies that the two subsystems are independent and so are free of correlations with one another.

The second postulate is the correspondence postulate which states that some (but not all) of the linear Hermitian operators that exist on a Hilbert space, which have complete orthonormal sets of eigenvectors (eigenfunctions), correspond to observables of a physical system. Note that due to a set of superselection rules (Wick et al., 1952), not all operators have observables. Furthermore, not all observables have operators as shown by Park and Margenau (1968) for the case of certain simultaneous measurements on a system. In IQT as with QM, operators, by which measurements of observables are made, can be represented by Hermitian matrices.

The state preparation postulate directly associates the physical state of the system with a well-defined method of preparation which allows a direct correspondence of the state with a density operator $\rho$ on the Hilbert space. The $\rho$ operator is linear, self-adjoint, non-negative definite, and unit trace and contains all physical predictions regarding measurements subsequent to the preparation of the state. Hence $\rho$ is also known as the state operator of the system.

The fourth postulate is the mean value postulate. It states that to every ensemble of measurements performed on identically and unambiguously prepared replicas of a system, there exists a real linear functional (function of an operator) $m(P)$ that can be applied to every Hermitian operator $P$ of the system such that if $P$ corresponds to an observable property $\overline{P}$, $m(P)$ is the arithmetic mean $\langle P \rangle$ of the ensemble of measurements. Given that the state of the
system is represented by a density operator \( \rho \), the functional \( m(P) \) is the trace operator, the mean or expectation value becomes

\[
\langle P \rangle = m(P) = \text{Tr}(\rho P)
\]  

(1.13)

It should be noted that to determine \( \langle P \rangle \) if \( \rho \) is not known, the number of identically prepared replicas one must use and the number of measurements one must make are infinite. However, if \( \rho \) is known, the fourth postulate guarantees that an average value of a system observable exists and can be determined by means of the trace operator.

The fifth and final postulate, the dynamical postulate, governs how a system evolves in time while allowing increases in entropy. For a system consisting of a single elementary constituent of matter i.e., a single particle, a single assembly of indistinguishable particles, or a single field the state operator \( \rho \) evolves according to\(^6\)

\[
\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{\tau} D
\]

where \([H, \rho] = H\rho - \rho H\); \( \tau \) is a scalar time constant or functional, and \( D \) is the dissipation operator. A lower bound for \( \tau \) and, thus, an upper bound on \( D/\tau \) has been established from the time-energy Heisenberg uncertainty relation (Beretta, 2010). The operator \( D \) allows the values of the state operator to change with time along a path of locally greatest entropy increase, subject to a set of constraints e.g., for a non-reactive system with constant system energy. Note that if \( D \) is zero, one is left with the von Neumann form (equation (1.8)) of the time-dependent Schrödinger equation (equation (1.5)) of QM. However, the above equation is more general in that both reversible and irreversible thermodynamic processes are represented. In addition,

---

5 At a given instant of time, \( \rho \) is a representation of the state of a system which catalogues how the energy of the system is distributed amongst the various energy eigenlevels of the system. This state operator is based on a homogeneous ensemble of identical systems, identically prepared, i.e. on an unambiguous preparation (Hatsopoulos and Gyftopoulos, 1976). This contrasts with the state operator of QSM, which is based on a heterogeneous ensemble of identical systems, not identically prepared, i.e. on an ambiguous preparation. The former leads to a true unification of thermodynamics and mechanics while the latter results merely in a bridging with a built-in violation of the Second Law of Thermodynamics, i.e. a perpetual motion machine of the second kind.

6 Equation (1.14) implies the First Law because as is proven in Beretta (1984), each of the generators (e.g., the identity and Hamiltonian operators) of the motion (i.e., the evolution or change in state of the system) is also a constant of the motion of the system, which in turn shows that \( \langle E \rangle = \text{Tr}(\rho H) \) is conserved and that \( \Delta \langle E \rangle \) in any adiabatic process is uniquely related to the amount of work involved in the process. Furthermore, equation (1.14) implies the second law because as is also proven in Beretta (1984), for given finite mean values of the generators of the motion, a system admits of one and only one stable equilibrium state. This, however, is simply a generalization of the second law as stated by Hatsopoulos and Gyftopoulos (1976). In addition, the dynamical postulate transforms the second law from a phenomenological law to one which is fundamental in the same sense that the postulates (or laws) of QM are fundamental, resulting, along with the general reconciliation of the kinematics found in Hatsopoulos and Gyftopoulos (1976), in a true unification (not simply bridging) of QM and ET.
processes may begin arbitrarily far from thermodynamic equilibrium. The specific details of the formulation of $D$ will be discussed in the next chapter.

In the years since its first introduction, further contributions to the theory of IQT have been made. A brief outline of the development of IQT is given in Table 1.1.

**Table 1.1 – Brief outline of the development of IQT.**

<table>
<thead>
<tr>
<th>Entropy formulated in terms of the concept of available energy; Restatement of the Second Law</th>
<th>(Hatsopoulos, Keenan, 1965)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Existence and uniqueness of stable equilibrium states</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The Unified Quantum Theory of Mechanics and Thermodynamics (IQT)</th>
<th>(Hatsopoulos, Gytopoulos, 1976)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Discovery of non-statistical quantum mechanical density operators more general than wave functions.</td>
<td></td>
</tr>
<tr>
<td>• Extension, without the use of statistical probabilities, of the ideas of QM to all states of Thermodynamics beyond those of zero entropy.</td>
<td></td>
</tr>
<tr>
<td>• Extension of ET ideas to all QM phenomena.</td>
<td></td>
</tr>
<tr>
<td>• Resolution of a number of paradoxes/dilemmas resulting from attempts to rationalize the relationship between mechanics and thermodynamics.</td>
<td></td>
</tr>
<tr>
<td>• The entropy of Thermodynamics is established as a non-statistical property of matter in any state, not just a stable equilibrium state.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A more complete equation of motion</th>
<th>(Beretta, 1981)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Encompasses the Schrödinger equation of motion as a special case and replaces the von Neumann equation of motion.</td>
<td></td>
</tr>
<tr>
<td>• Able to predict the evolution in time of a system’s state be it mechanical or thermodynamic.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>A non-quantal exposition of thermodynamics</th>
<th>(Gyftopoulos, Beretta, 1991, 2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Thermodynamics applies to all systems, large and small, including single particle systems.</td>
<td></td>
</tr>
<tr>
<td>• Thermodynamics applies to all states i.e., both stable equilibrium and not stable equilibrium states.</td>
<td></td>
</tr>
<tr>
<td>• Entropy is a fundamental property of each constituent of matter; its smallest value is zero for purely mechanical states and &gt; 0 for thermodynamic states.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermodynamic definition/quantum expression of entropy.</th>
<th>(Gyftopoulos and Çubukçu, 1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Based on the QT, a set of eight criteria are established which the entropy of Thermodynamics must meet.</td>
<td></td>
</tr>
</tbody>
</table>
- All expressions found in the literature fail one or more of these criteria except the one which comes from the QT.

Presentation of quantum-theoretic shapes in terms of spatial coordinates within the context of IQT
- Assertion that independent of any statistical considerations, entropy is a measure of the quantum theoretic shape of the constituents of any system in any state.
- Assertion that irreversibility results from the spontaneous change of the quantum-theoretic shapes of constituents as they conform to the external and internal forces acting upon them.

(Gyftopoulos, von Spakovsky, 2003)

Non-statistical development of the Onsager reciprocal relations and the Callen fluctuation-dissipation relations for non-equilibrium
- Demonstration that arguments based on statistical fluctuations, time reversal, and the principle of microscopic reversibility play no role in the thermodynamic theory of irreversible processes.

(Beretta, 1987)

Application of IQT to bounded systems
- Beretta models a single two-level atom which interacts with a quantum electromagnetic field and suggests that discrepancies between experiment and theoretical predictions are due to an irreversible atomic relaxation to stable equilibrium.
- Çubukçu models the absorption rate behavior of transmitted light by (five-level) vapor Rb atoms in a magnetic field and predicts the damping effects due to the irreversible relaxation of spin states to equilibrium.

(Beretta, 1985; Çubukçu, 1993)

Application of IQT to unbounded systems
- H₂ storage on C-nanotubes modeled in 3D

(Smith et al., 2010; von Spakovsky and Smith, 2008;

### 1.7 Research Objectives, Original Contributions and Practical Impacts

There are two principal goals to be accomplished by the present doctoral work. The first is to develop a practical approach for applying IQT to the non-equilibrium modeling of unbounded gaseous systems at the nanoscale. Once developed, this approach will be applied to a real-world problem of current interest. The one chosen for this research is that of modeling in 3D the storage of hydrogen on a carbon nanotube. The second goal is to extend the theory of IQT by augmenting the applicability of its equation of motion to account for both heat and mass...
interactions at least from a phenomenological standpoint. At present, the equation of motion (equation (1.14)) originally developed by Beretta (Beretta, 1981; Beretta et al., 1984) and then extended to multiple elementary constituents (Beretta, Gyftopoulos and Park, 1985) applies either to an isolated system or a non-isolated system undergoing a work interaction. Beretta has since extended the equation to phenomenologically deal with heat interactions (Beretta, 2009a). However, there are drawbacks to this particular extension which will be addressed here. In addition there is lacking an extension of IQT theory that describes mass interactions.

In order to accomplish these two principal goals, the following set of major tasks is envisioned:

- Understand the underlying theory of IQT both in terms of its non-quantal and quantal expositions and its relation to QSM and QT; this entails understanding both the stationary aspects of IQT, which for example lead directly from a set of elementary quantum mechanical models to the property relations of ET via the Maximum Entropy Principle, as well as the non-stationary aspects of the theory, which deal with irreversible evolutions in state even far from equilibrium;

- Develop the elementary quantum mechanical models for modeling the movement of hydrogen molecules contained in a tank at the center of which is a carbon nanotube; these models should account for both external (translation) and internal (e.g., vibration, rotation, etc.) degrees of freedom as well as for the interactions between hydrogen molecules and the hydrogen molecules and the carbon atoms;

- Understand the bond and geometric aspects of carbon nanotubes and then mathematically construct different kinds of carbon nanotubes to be placed at the center of the tank;

- Establish the energy eigenstructure of the hydrogen and carbon in the tank by first defining the multi-body energy eigenvalue problem for the system (i.e., for the hydrogen and carbon contained in the tank) and a set of two-body energy-eigenvalue problems which closely approximate the multi-body problem for the system;

- Implement and validate a finite element approach for solving the translational two-body energy eigenvalue problems and do so for complex geometries using an unstructured finite element grid;
Develop a scheme for combining the two-body problems and the solutions for the internal degrees of freedom as well as a scheme for approximating an infinitely large number of energy eigenlevels with a finite set that closely reproduces the results one would expect to obtain with the infinite set;

Implement and validate the IQT equation of motion for this system using the energy structure established in the previous tasks and a number of different initial states far from equilibrium; predict the thermodynamic paths taken as the system relaxes to stable equilibrium as well as the “limit cycle”, which is the lowest entropy state (the so-called “ancestral” or primordial” state) from which all succeeding states of the system originate;

Compare the results of this dynamic, non-equilibrium thermodynamic simulation with experimental data and/or comparable Monte Carlo (MC) and Molecular Dynamic (MD) simulations found in the literature. This will be done as a further step of validation although finding comparable results may prove difficult if not impossible;

Understand the derivation of the equation of motion developed by Beretta (2009a), which contains the additional term for the heat interaction and study its behavior and the basis for the phenomenological terms (the non-equilibrium temperatures) which it contains;

Address the drawbacks to the Beretta heat interaction term. Suggest and implement modifications which resolve the drawbacks;

Modify the Beretta equation of motion by developing a mass interaction term and study its behavior and the basis for the phenomenological terms which it contains;

Although the theory of QT is more than three decades old, the limited attention it has received over the years has resulted in the discipline being in many respects still in a developmental stage. There are yet many opportunities for doing ground-level research, especially in terms of applications both to bounded and unbounded systems. Thus, the two principal goals envisioned above constitute new and original contributions to the literature. To date, no one has dynamically and quantum thermodynamically modeled the non-equilibrium behavior of unbounded systems in general and of hydrogen storage on carbon nanotubes in particular. To do so practically, a number of technical issues must be addressed. These include but are not limited to, for example, closely approximating an infinite with a finite number of
eigenlevels, developing effective ways of dealing with multi-body interactions, pushing well beyond the ground energy level limit of current equilibrium-based approaches e.g., DFT (Parr and Yang, 1989), Coupled Cluster Theory (Hampel and Werner, 1996; Schutz, 2002; Crawford, 2006; Russ and Crawford, 2004), etc. If successful, the way to the design of non-equilibrium nanoscale gas systems using the concept of entropy minimization, a very powerful tool already used with macroscale systems, will be open. It will also provide the basis for future work on modeling both liquid and solid nanoscale systems, which in turn will lead to the of design material-interface systems from a non-equilibrium perspective, beginning at an atomistic level.

Finally, this research will attempt an extension of the theory of IQT by phenomenologically incorporating a mass interaction term into the Beretta equation of motion. With such an extension and the modification of the previous work by Beretta (2009a), the basis for studying the non-equilibrium behavior of nanoscale systems experiencing non-work (both heat and mass) interactions will be complete, thus, expanding the types of processes that can now be modeled to those of open systems.
Chapter 2 - Literature Review

2.1 Development of Intrinsic Quantum Thermodynamics

2.1.1 Theoretical Developments

2.1.1.1 Hatsopoulos-Gyftopoulos Paradigm

The first efforts of what would later be called Intrinsic Quantum Thermodynamics (IQT) began with the work of J. H. Keenan and his development of the concept of “availability” or “available energy” in the 1940’s. Power companies had requested a straightforward and objective way of valuing the energy they produced from various sources. Keenan, through a careful study of the ideas of Josiah W. Gibbs concerning entropy, came to see that not all energy has the same ability to do work. Keenan realized that the ability of a given amount of energy to do work, which he later termed as availability, would not only provide a simple guide for pricing energy but also could serve as a fundamental way to describe the concept of entropy, a description that still serves as an important foundational idea within IQT.

The perception that there were inconsistencies in the way the concept of entropy is viewed and handled motivated Hatsopoulos (Hatsopoulos and Keenan 1965) to develop an important restatement of the Second Law of Thermodynamics. Hatsopoulos asserted that all that could be said about the Second Law with its implications of irreversibility could be contained in the idea that there exist unique and stable equilibrium states toward which all systems tend to evolve.

The comprehensive and foundational work for IQT was then presented in 1976 by Hatsopoulos and Gyftopoulos (1976a,b,c,d). Their accomplishments include i) the extension, without the use of statistical probabilities, of the ideas of Quantum Mechanics (QM) to all states of Thermodynamics beyond those of zero entropy; ii) the extension of classical (equilibrium) thermodynamic (ET) ideas to all quantum theory phenomena; and iii) the resolution of a number of paradoxes resulting from attempts to rationalize the relationship between mechanics and thermodynamics. Their work is based on rigorous statements of the postulates on which QM is based. Included are statements for quantum system definition, the correspondence between observables and operators, state preparations, the existence of mean values for observables obtained via measurements of identically prepared ensembles, and the existence of unique stable equilibrium states which is the essence of the Second Law of Thermodynamics. Details of these
will be discussed subsequently. Their dynamical postulate contains not only the traditional
definition of the time dependent Schrödinger equation but also asserts the existence of an
equation of motion that describes how the entropy for quantum systems evolves in time. In
contrast, the von Neumann equation,

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H,\rho]$$

(2.1)

which is the density operator version of the Schrödinger equation and the starting point for most
Quantum Statistical Mechanical (QSM) derivations, is inadequate for describing systems with
changes in entropy. The main reason is that the von Neumann equation is reversible and limited
to unitary transformations and as such is not able to change the eigenvalues of the state matrix,
which is required if the entropy is to change.

A restated, updated formulation of the postulates is found in Beretta et al. (1984). All
arguments presented are based on the use of quantum mechanical density operators and on a
rigid adherence to the idea that density operators correspond to an indivisible state of the system
and not a collection of individual pure states statistically grouped together as QSM customarily
assumes.

In addition to the postulates of IQT, Hatsopoulos and Gyftopoulos (1976a,b,c,d) give a
set of strict definitions for the basic thermodynamic concepts on which IQT is based. The
definitions are used to prevent unneeded compromises, circular arguments, or unnecessary
restrictions that may lead to ambiguities or inconsistencies. Rigorous definitions for
thermodynamic systems, system properties, system states, and processes are presented.

2.1.1.2 Introduction of the IQT Equation of Motion

A crucial piece of the IQT theory, the complete equation of motion for an IQT system
where the entropy of the system is a function of time, was developed by Beretta (1981). Using
the mathematics of manifolds with the needed projections and applied constraints, Beretta
developed an equation that describes how the entropy for the system changes with time due to
the energy being continuously redistributed within the energy eigenstructure of the system. The
assumption that is made in is that the system follows a path of steepest local entropy increase
(ascent) on the way to stable equilibrium. The constraints that must be satisfied are that of
maintaining the energy of the system constant and keeping the trace of the density operator equal to unity. A schematic of the geometrical argument is shown in Figure 2.1.

Figure 2.1. Geometric depiction of the constrained steepest entropy ascent problem solved by Beretta described in e.g. Beretta (1981) and Beretta (2009a).

The vector $b$ represents the direction of steepest entropy increase at a given instant in time. The manifold $L$ is a surface that is spanned by the two mentioned constraints which are labeled as $g_0$ and $g_1$. What is desired is to obtain the portion of $b$ that is independent of the constraints, that is, the component of $b$ that is perpendicular to $L$. The perpendicular component $b_\perp$ is the component of greatest entropy increase subject to the constraints, which is then recast in terms of the generators of the motion. For an isolated, non-reacting system, the generators of the motion are the identity operator $I$ and the Hamiltonian operator $H$.

The operator resulting from this construction is a dissipation operator which predicts how the system entropy increases in time. Beretta expresses this dissipation operator in his initial work as a ratio of determinants (see Beretta 1981; Beretta et al. 1984; Beretta 1986; Beretta 2006a,b; Beretta 2009a for details). For a system consisting of a single elementary constituent of matter i.e., a single particle, a single assembly of indistinguishable particles, or a single field, the dissipation operator $D$ can be represented as

$$D = \left| \begin{array}{ccc} -\frac{1}{2}\{s,\rho\} & \rho & \frac{1}{2}\{H,\rho\} \\ \text{Tr}(\rho S) & 1 & \text{Tr}(\rho H) \\ \text{Tr}(\rho HS) & \text{Tr}(\rho H) & \text{Tr}(\rho H^2) \end{array} \right|$$

(2.2)

where the determinant in the denominator is a Gram determinant which guarantees the linear independence of the generators of the motion for values of the determinant greater than zero.
(Beretta, 1984). The brackets in the second determinant represent the anti-commutator so that these two bracketed terms are written as
\[
\frac{1}{2}\{H, \rho\} = \frac{1}{2}(H\rho + \rho H)
\]  
(2.3)
\[
\frac{1}{2}\{S, \rho\} = \frac{1}{2}(S\rho + \rho S)
\]  
(2.4)
Since \( S \) commutes with \( \rho \) and \( S \) is the dimensionless entropy operator given by
\[
S = -B \ln \rho
\]  
(2.5)
where \( B \) is an idempotent operator found from \( \rho \) by substituting in its spectral expansion each nonzero eigenvalue with unity, equation (2.5) can be rewritten as
\[
\frac{1}{2}\{S, \rho\} = \frac{1}{2}(2S\rho) = -\rho \ln \rho
\]  
(2.6)
Substitution into equation (2.4) yields
\[
D = \begin{bmatrix}
\rho \ln \rho & \rho & \frac{1}{2}\{H, \rho\} \\
\text{Tr}(\rho \ln \rho) & 1 & \text{Tr}(\rho H) \\
\text{Tr}(\rho H \ln \rho) & \text{Tr}(\rho H) & \text{Tr}(\rho H^2)
\end{bmatrix}
\]  
(2.7)
The equation of motion to which this dissipation operator belongs is then the Beretta equation written as
\[
\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{\tau} D
\]  
(2.8)
where \( \tau \) is a scalar time constant or functional. This equation is more general than the von Neumann equation of motion, is nonlinear and is able to predict the evolution of state of an isolated system regardless of whether or not the states involved are mechanical or thermodynamic and is fully consistent with the laws of thermodynamics including the Second Law.

Since his original dissertation (Beretta, 1981) and 1984 paper (Beretta et al., 1984), Beretta has reformulated his presentation of the IQT equation of motion (Beretta, 2001, 2006a,b, 2007).

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7 Note that as will be shown in Chapter 3, \( \rho \) and \( H \) may or may not commute.
8 Note, that a lower bound for \( \tau \) and, thus, an upper bound on \( D \) has been established from the time-energy Heisenberg uncertainty relation (Beretta, 2010).
In addition, his equation has been derived independently by Gheorghiu-Sverschevski (2001) using variational principles. In the derivation by Gheorghiu-Sverschevski the constraints are identical to that of the Beretta equation, i.e., all probabilities of the density matrix must add to unity and the energy remain constant when the system is isolated. A Lagrangian is formed by combining Lagrange multipliers with these constraints and the Lagrangian is then maximized yielding an equivalent expression to Beretta’s dynamical equation. A succinct summary on the most recent notation of IQT is found in Beretta (2009a) and summarized in Chapter 3.

2.1.1.3 In Support of the IQT Viewpoint

Bolstering IQT from a quantum theoretical viewpoint has been the work of Park (1968, 1988). Most of his contributions involve explaining the inconsistencies which exist relative to the basic assumptions underpinning QSM. For instance, the argument is made that any attempt to assemble a grouping of individual system states, may, in fact, not result in the unified collection having the properties of a physical state, an observation also noted by Schrödinger (1936). In other words, the concept of the state of the system, a bedrock of physical thought, is lost in QSM since the state of the ensemble may no longer correspond to the state of the system. This is the case when the states of the identical systems of an ensemble are ambiguously prepared, that is, are not all in the same state. Moreover, statistically grouping pure quantum states that have no entropy into a collective state that is said to possess entropy as is routinely done in QSM, leads to fundamental inconsistencies. Some texts, like Liboff (1980), concede that in QSM the concept of state no longer applies. But without a state of the system, any consistent measurement of physical quantities of interest is only meaningful for the ensemble and not the system.

2.1.1.4 Extension of Thermodynamics to All States

Another development of IQT is the extension of thermodynamics to all states, even non-equilibrium states far from stable equilibrium. Using the principles of IQT, Beretta (1986, 2009ab, 2010) and Beretta and Gytopoulos (2004) present a non-statistical development of the
Onsager reciprocity relations (Onsager, 1931a,b; Onsager and Machlup, 1953) and the Callen fluctuation-dissipation relations (Callen and Welton, 1951; Greene and Callen, 1951; Callen, Barasch, and Jackson, 1952). The results are general and hold for systems that are near or far from stable equilibrium. The Onsager reciprocity relations are seen to follow naturally from the inherent symmetry of the matrices on which the Beretta dissipation operator in the Beretta equation is based. The results of the fluctuation-dissipation theorem are shown to stem from the probability distributions associated with observables and the covariances (i.e., “co-dispersions”) between them that are embedded within the structure of IQT and all without the need for external statistical models such as those which come from Statistical Mechanics (SM). The papers demonstrate that descriptions based on statistical fluctuations, time symmetry, and microscopic reversibility are not required and, therefore, can be assumed to play no role in the theory of irreversible processes.

The basis of these derivations proceeds by starting with the idea that any non-equilibrium density operator $\rho$ can be written in the following form consisting of pairs of affinities conjugated with corresponding observables, i.e.,

$$\rho = \frac{B \exp(-\sum_j f_j X_j)}{\text{Tr}(B \exp(-\sum_j f_j X_j))}$$  \hspace{1cm} (2.9)

where $B$ is again the well-defined idempotent operator used in equation (2.5) above and needed to maintain the entropy operator as positive semi-definite. The $f_j$ are the affinities or “forces”, the $X_j$ the observables, and the set $\{X_j\}$ a so-called quorum of observables, the mean values of which are needed to fully determine $\rho$ (Beretta, 2009a,b; Band and Park, 1970, 1971a, 1971b). The expectation (mean) values of these observables can be written as

$$\langle X_j \rangle = \text{Tr}(\rho X_j)$$  \hspace{1cm} (2.10)

so that the entropy is given by

$$\langle S \rangle = k_b f_0 + k_b \sum_j f_j \langle X_j \rangle$$  \hspace{1cm} (2.11)

where $k_b$ is Boltzmann’s constant and $f_0$ a generalized log-partition function expressed as (Beretta, 2010)

$$f_0 = k_b \ln \left( \text{Tr} \left( B \exp \left( -\sum_j f_j \langle X_j \rangle / k_b \right) \right) \right)$$  \hspace{1cm} (2.12)
The generalized affinity or force can then be written in terms of its conjugate observable such that
\[ k_b f_j = \left( \frac{\partial \langle S \rangle}{\partial \langle X_j \rangle} \right)_{X_i \neq j} \tag{2.13} \]

Now, each observable is affected by dissipation effects in the system’s evolution of state. The dissipative part of the time rate of change for an observable \( \langle X_i \rangle_D \) can be identified and written as a linear function of the affinities such that
\[ \langle X_i \rangle_D = \sum_j f_j L_{ij}(\rho) \tag{2.14} \]

The \( L_{ij} \) in this last expression are coefficients known as generalized conductivities and are nonlinearly dependent on \( \rho \), namely,
\[ L_{ij}(\rho) = \frac{1}{\tau} \left( \frac{\langle \Delta X_i \Delta X_j \rangle}{\langle \Delta X_i \Delta H \rangle} \frac{\langle \Delta H \Delta X_j \rangle}{\langle \Delta H \Delta H \rangle} \right) \tag{2.15} \]

The term \( \langle \Delta H \Delta H \rangle \) represents the variance of the Hamiltonian operator, while the other terms are the covariances between pairs of observables \( X_i \) and \( X_j \) as well as between the Hamiltonian and the observables. The terms in the determinants are arranged symmetrically so that the Onsager reciprocity theorem, which describes the relationship between two simultaneously occurring irreversible rate processes, follows as a result. Thus,
\[ L_{ij} = L_{ji} \tag{2.16} \]
a result which is seen to hold whether the system is near or far from stable equilibrium.

Another result among others of the IQT development is that the entropy generation rate due to the coupling between two rate processes can be written in terms of their corresponding forces such that
\[ \frac{d\langle S \rangle}{dt} = \dot{S}_{gen} = k_b \sum_i \sum_j f_i f_j L_{ij}(\rho) \tag{2.17} \]

In 2004, the IQT derivation of the Onsager relations was applied to a chemically reacting system in an isolated container (Beretta and Gyftopoulos, 2004). Derived are the conditions needed for chemical equilibrium. In addition, it is shown how IQT can be used to find the near-equilibrium Onsager reciprocity relations for the reactions as well as other non-equilibrium properties. The
paper is an important example of how IQT can be directly compared to the standard theory for the kinetics of chemical reactions.

The use of IQT carries the added bonus of offering a way of predicting physical properties that are well away from stable equilibrium, properties that cannot be predicted using traditional methods but that may be verifiable through experiments. A possible application may be the derivation using IQT of the Arrhenius equations which describe how the rate constants of chemical reactions depend on temperature. If such is the case, chemical reactions studied far from equilibrium may provide direct experimental evidence for the veracity of IQT. Work in this direction is currently underway by Beretta and von Spakovsky.

2.1.1.5 Definition of the Entropy of Thermodynamics

An additional important development in IQT is that of Gyftopoulos and Çubukçu (1997). The authors examine whether or not all of the numerous expressions for entropy, which proliferate the literature, are acceptable as the entropy of thermodynamics. Their definitive answer is an emphatic “no”, an answer at which the authors arrive by establishing a set of eight criteria that the entropy of thermodynamics must meet. These criteria are based on the rigorous exigencies of IQT and appear in Table 2.1. They are used to screen the most likely candidate expressions, namely, the QM expressions by Daróczy (1970), i.e.,

$$S_D = \frac{1}{2^{1-a} - 1} (\text{Tr} \rho^a - 1)$$  \hspace{1cm} (2.18)

where \(a\) is greater than zero but not equal to 1, the Hartley entropy, i.e.,

$$S_H = k_B \ln N(\rho)$$  \hspace{1cm} (2.19)

where \(N(\rho)\) is the number of positive eigenvalues of \(\rho\), the infinite norm entropy, i.e.,

$$S_\infty = k_B \ln \|\rho\|_\infty$$  \hspace{1cm} (2.20)

where \(\|\rho\|_\infty\) is the largest eigenvalue of \(\rho\), the Rényi entropy

$$S_R = \frac{k_B}{1-a} (\text{Tr} \rho^a)$$  \hspace{1cm} (2.21)
where \( a \) is greater than zero but not equal to 1, and the IQT entropy (Hatsopoulos and Gyftopoulos, 1976; Gyftopoulos and Çubukçu (1997))\(^9\), which uses the density or “state” operator of IQT with the von Neumann expression for the entropy, i.e.,

\[
S_v = -k_B \text{Tr}(\rho \ln \rho) \tag{2.22}
\]

Table 2.1. Eight criteria which the entropy of thermodynamics must satisfy (Gyftopoulos and Çubukçu, 1997).

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The expression must be well-defined for every system regardless of size and every state whether metastable, unstable, or stable equilibrium as well as non-equilibrium, steady, and unsteady states.</td>
</tr>
<tr>
<td>2</td>
<td>The expression must not vary in all reversible adiabatic processes yet must increase in all irreversible adiabatic processes.</td>
</tr>
<tr>
<td>3</td>
<td>The expression must be additive for all states and systems.</td>
</tr>
<tr>
<td>4</td>
<td>The expression must be non-negative and must vanish for all states encountered in mechanics.</td>
</tr>
<tr>
<td>5</td>
<td>For given values of the energy, amounts ( \bar{n} ) of constituents, and parameters ( \bar{\beta} ), there should be one and only one state which corresponds to the largest value of the expression.</td>
</tr>
<tr>
<td>6</td>
<td>For given values of ( \bar{n} ) and ( \bar{\beta} ), the entropy-energy curve of stable equilibrium states must be concave and smooth.</td>
</tr>
<tr>
<td>7</td>
<td>For a composite system ( C ) consisting of two subsystems ( A ) and ( B ), the expression must be such that the constrained maximization of the entropy for ( C ) (criterion 5) results in identical thermodynamic potentials (e.g., pressure, temperature, and chemical potentials) for all three systems ( A ), ( B ), and ( C ).</td>
</tr>
<tr>
<td>8</td>
<td>For states in stable equilibrium, the expression must reduce to experimentally established relations (e.g., those for ideal gases), which express the entropy in terms of the values of the energy, ( \bar{n} ) and ( \bar{\beta} ).</td>
</tr>
</tbody>
</table>

Expressions for entropy based on temperature and heat (typical of ET) are excluded because they only apply to stable equilibrium states (fail criterion 1). Those which come from statistical mechanics are not acceptable because they are based on statistical (i.e., subjective) as opposed to quantal (i.e., inherent) probabilities and the entropy which results is, therefore, not a fundamental property of matter. Expressions which come from QSM and depend on variables other than the eigenvalues of the density operator are also excluded because they fail the criterion that the entropy must be invariant or increase (fail criterion 2).

\(^9\) The original proof by Hatsopoulos and Gyftopoulos (1976) is completed and generalized in Gyftopoulos and Çubukçu (1997).
Of the expressions which are left (equations (2.18) to (2.22)), all but one fail one or more criteria. A summary of the criteria that are satisfied by these expressions for the entropy is given in Table 2.2. As can be seen, only the IQT entropy based on the von Neumann expression, \( S_v \), satisfies all 8 criteria (Gyftopoulos and Çubukçu, 1997).

**Table 2.2.** Assessment of the candidate expressions for the entropy of thermodynamics (Gyftopoulos and Çubukçu, 1997).

<table>
<thead>
<tr>
<th>Entropy Expression</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_D )</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_H )</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_{\infty} )</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S_R )</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>( S_v )</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

2.1.1.6 Required Characteristics of the Equation of Motion

In a vein similar to that of the Gyftopoulos and Çubukçu (1997) paper, Çubukçu (1993) in his doctoral dissertation develops nine characteristics that a satisfactory equation of motion should possess. The guidelines are then applied to several of the leading methods for modeling non-equilibrium quantum phenomena. The Beretta equation satisfies all the criteria while the others do not. A general equation of motion is given in the form of

\[
\frac{\partial \rho}{\partial t} = F(\rho, H)
\]  

(2.23)

where \( F \) is the right-hand-side of the equation of motion in operator form, operating on the density operator \( \rho \) and the Hamiltonian of the system. The list of characteristics, which this equation in general form must satisfy, appears in Table 2.3.

The characteristics listed in the table certainly are useful and reasonable in evaluating the equations of motion found in the literature. From a QT (not IQT) point of view there may be disagreement as to whether strict adherence on all points is required. It may be argued, for example, that since the master equation formalism of the Kossakowski-Sudarshan-Gorini-Lindblad (KSGL) equation (Kossakowski, 1972; Ingarden and Kossakowski, 1975; Lindblad,
Table 2.3 Characteristics that a satisfactory equation of motion should possess (Çubukçu, 1993).

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The equation of motion must preserve the Hermiticity of the state operator $\rho$, a requirement that all operators in physics must meet to ensure physical relevance. This requires that $F(\rho, H) = F(\rho, H)^*$ (2.24) Thus, an operator must be equal to its Hermitian conjugate.</td>
</tr>
<tr>
<td>2</td>
<td>The trace of $\rho$ must at all times equal unity so that all measurement probabilities add to 1.</td>
</tr>
<tr>
<td>3</td>
<td>For an isolated system, the energy must be conserved.</td>
</tr>
<tr>
<td>4</td>
<td>The entropy of an isolated system must not decrease and for many cases of interest, the entropy must increase.</td>
</tr>
<tr>
<td>5</td>
<td>$\rho$ must always be non-negative definite, i.e., $\rho \geq 0$ for all times.</td>
</tr>
<tr>
<td>6</td>
<td>The equation of motion must reduce to the von Neumann equation when the system is a pure state and the entropy is zero, i.e., $\frac{\partial \rho}{\partial t} = [\rho, H]$ (2.25)</td>
</tr>
<tr>
<td>7</td>
<td>Solutions of the equation of motion for a system that is a composite of two independent subsystems $A$ and $B$ should correspond with the results of separate equations of motion for subsystem $A$ and subsystem $B$. In this case, the density operator must evolve according to $\rho_{AB}(t) = \rho_A(t) \otimes \rho_B(t)$ (2.26) where $\otimes$ represents the matrix outer product and the operator $F_{AB}$ satisfies the relation $F_{AB}(\rho_{AB}, H_{AB}) = F_A(\rho_A, H_A) \otimes \rho_B + \rho_A \otimes F_B(\rho_B, H_B)$ (2.27)</td>
</tr>
<tr>
<td>8</td>
<td>A physically relevant solution to the equation of motion must exist and be unique for any initial condition $\rho(0)$.</td>
</tr>
<tr>
<td>9</td>
<td>The time evolution of the equation of motion must be consistent with experimental observations.</td>
</tr>
</tbody>
</table>

1976) and the Pauli master equation (e.g., Blum, 1996) are only valid going forward in time, the requirement that it obey characteristic 5, the non-negativity of $\rho$ going backwards in time, is not necessary. Since QT supposes that irreversibilities (dissipations) are in fact the build up and annihilation of correlations due to weak interactions with the environment, strict adherence to characteristic 3 (i.e., conserving the energy of the system) need not be observed. Furthermore, if the model is useful in describing experimental observations, characteristic 9 may be used as a
pretext to ignore rigorous enforcement of the other criteria. The lack of thermodynamic rigor, however, brings into question whether master equations based on QT correspond to valid notions of the irreversibilities which the system sees as its state relaxes to stable equilibrium.

2.1.1.7 IQT Shape of Entropy

Another theoretical development of note is that presented in Gyftopoulos and von Spakovskovsky (2003), namely, a pictorial visualization of the entropy of a system as a measure of the spatial shape of the constituents of a system. In the literature, the probability density function associated with measurement results of the spatial coordinates of the constituents of a system is oftentimes interpreted as the spatial shape of these constituents (Leighton, 1959; Brandt and Dahmen, 1995), and the shape is used to calculate atomic, molecular, and ionic radii (Slater, 1963) as well as explain the formation of various compounds. The probability density function of the spatial coordinates also enters into the evaluation of the entropy. The probability density indicates the likelihood of finding a particle at a given location and time within the system.

What Gyftopoulos and von Spakovskovsky (2003) demonstrate is that the closer the system is to stable equilibrium the smoother the shape of the probability density function becomes. The smoothness therefore can be taken as a graphical measure of the entropy for the system. For the examples illustrated, Gyftopoulos and von Spakovskovsky (2003) use density (i.e., state) operators \( \rho \) that are diagonal. The corresponding probability density function then has the form

\[
p(x) = \sum_{i=1}^{n} \rho_{ii} u_i^2(x)
\]

(2.28)

where the \( \rho_{ii} \) are the probability weightings along the diagonal of \( \rho \) and the \( u_i(x) \) are the energy eigenfunctions of \( \rho \).

The authors present a number of 1D and 2D quantum theoretic shapes for several types of simple systems. In each case the distributions are constructed from linear combinations of the eigenfunctions for the system as calculated from the stationary Schrödinger equation (i.e., from the energy eigenvalue problem which establishes the energy eigenstructure of the system). The initial shape of the state function can be arbitrarily chosen and represents a preparation of the state of the system. For the example, for a structureless particle in a 1D infinite square well, the initial non-equilibrium state is described by the following diagonal density or state operator \( \rho \) (Gyftopoulos and von Spakovskovsky, 2003):
The only diagonal elements $\rho_{ii}$ not equal to zero are $\rho_{22} = 0.1$, $\rho_{33} = 0.2$ and $\rho_{88} = 0.7$ and must sum to unity as they represent probabilities. These elements serve as the weighting terms when summing the contribution of each 1D energy eigenfunction $u_i(x)$ to the probability density function, $p(x)$. For simplicity, any contributions from off diagonal terms, terms which are responsible for interference, i.e., coherence effects between the eigenfunctions, have been suppressed.

The probability density function associated with this density or state operator can be written at a given instant of time as

$$p(x) = \sum_{i=1}^{8} \rho_{ii} u_i^2(x)$$

(2.30)

Substituting the energy eigenfunction solutions for this system results in

$$p(x)/(2d) = 0.1\sin^2(2\pi x/d) + 0.2\cos^2(3\pi x/d) + 0.7\sin^2(8\pi x/d)$$

(2.31)

where $2d$ is the width of the well. The entropy $\langle S \rangle$ and energy $\langle E \rangle$ of this 1D system are then determined from

$$\langle S \rangle = -k_b \sum_{i=1}^{8} \rho_{ii} \ln \rho_{ii} = -k_b [0.1\ln(0.1) + 0.2\ln(0.2) + 0.7\ln(0.7)] = 0.802k_b$$

(2.32)

and

$$\langle E \rangle = (h^2/8Md^2)[0.1(4) + 0.2(9) + 0.7(64)] = 47h^2/8Md^2$$

(2.33)

Where $k_b$ is Boltzmann’s constant, $h$ is Planck’s constant and $M$ is the mass of the particle. Holding the energy constant, the authors then maximize the entropy of the system so that it reaches a value of

$$\langle S \rangle = k_b \ln Q + \langle E \rangle/T = 2.65k_b$$

(2.34)

Here $T$ is the system temperature at stable equilibrium and the value of the partition function $Q$ appearing in equation (2.34) is given by (Hatsopoulos and Gyftopoulos, 1979; Gyftopoulos and von Spakovsky, 2003)
\[ Q = \sum_{n=1}^{\infty} \exp(-\alpha n^2) \equiv (2\pi M k_b T d^2 / h^2)^{1/2} = 8.6 \]  

(2.35)

The state associated with equation (2.35) is the unique stable equilibrium state corresponding to that predicted by the Second Law of Thermodynamics. The probability density function corresponding to this state is written as

\[ p(x) = \frac{1}{2Q/d} \left( \sum_{n=\text{odd}}^{\infty} \cos^2(n\pi x/d) \exp(-\alpha n^2) + \sum_{n=\text{even}}^{\infty} \sin^2(n\pi x/d) \exp(-\alpha n^2) \right) \]  

(2.36)

where

\[ \alpha = \frac{\hbar^2}{8Md^2k_bT} \]  

(2.37)

Using equations (2.31) and (2.36), plots of the quantum theoretic shapes for both the non-equilibrium and stable equilibrium states are shown in Figure 2.2. Arbitrary dimensionless units are used for the spatial coordinates and the probability density function. The very wavy shape seen in Figure 2.2a reflects the non-equilibrium nature of the state of the system with the particle more likely located in regions with the higher peaks. At stable equilibrium and maximum entropy (Figure 2.2b), the peaks and troughs disappear as the shape smoothes out to a near uniform distribution.

![Figure 2.2. Plot of the quantum theoretic shapes of a single particle in a 1D infinite well for a) the non-equilibrium state and b) the stable equilibrium state (Gyftopoulos and von Spakovsky, 2003). Reprinted with permission, ASME.](image)

Results for a structureless particle in a 2D infinite square well are shown in Figure 2.3. The initial state of the system at an energy of

\[ \langle E \rangle = 94\hbar^2 / 8Md^2 \]  

(2.38)
is in a non-equilibrium state. The associated quantum theoretic shape appears in Figure 2.3a and exhibits many irregularities (i.e., peaks and troughs). The stable equilibrium is shown in Figure 2.3b. As in the 1D case, the quantum theoretic shape becomes smoother and more uniform as the maximum entropy of the system at the same energy is approached.

**Figure 2.3.** Non-equilibrium and equilibrium quantum theoretic shapes of the structureless particle in the 2-D infinite square well (Gyftopoulos and von Spakovsky, 2003). Reprinted with permission, ASME.

### 2.1.1.8 Non-quantal Exposition of IQT

One final theoretical development of IQT is its non-quantal exposition developed by Gyftopoulos and Beretta (1991, 2005) and based on the fundamentals laid down by Hatsopoulos and Gyftopoulos (1976a,b,c,d). Emphasized in great detail are the basic concepts of IQT and equilibrium thermodynamics in general. In addition to thermodynamic system, state, property, interaction, and process definitions and numerous other developments, assertions are made that i) thermodynamics applies to all systems large and small, including one particle systems; ii) that it applies to all states, i.e., stable equilibrium and not stable equilibrium states (non-equilibrium, metastable and unstable equilibrium, steady and unsteady states); and iii) entropy is a fundamental property of each constituent of matter, with its smallest value being zero for purely mechanical states and greater than zero for all other thermodynamics states.
2.1.2 Experimental Support for IQT

2.1.2.1 Two-Level Quantum Spin-1/2 System and the IQT Equation of Motion

Although no experiments to date have been done directly to verify or substantiate IQT, a few papers have suggested experiments that might be used to do so in the laboratory. For example, Beretta (1985a) applied the equation of motion of IQT to a two-level quantum spin system of an isolated particle in three dimensions. The system is an example of a single particle system which IQT predicts will evolve irreversibly over time if initially in a non-equilibrium state. Geometrically, the system can be mapped to a sphere of unit radius also known as a Bloch sphere. Two of these spheres for such a two-level system appear in Figure 2.4. The first qualitatively illustrates the evolution predicted by QM and the second that predicted by IQT. Such a system is modeled experimentally as a simple nuclear resonance system and could be used to verify the assertions of IQT.

The thermodynamic state of the system is represented by \( \mathbf{r}(t) \) (i.e., is related to the density or state operator \( \rho \) of IQT), which is a radius vector whose length and rotational position can vary with time. The lowest energy level (the ground state energy) is on the \( z \)-axis at the bottom of each sphere, while the highest (the maximum energy state) is at the top of each sphere. The symbol \( h \) is the direction of an external magnetic field. In moving in the \( x-y \) plane, any state on the surface of the spheres, i.e., at unit radius, is one of zero entropy, while those in the interiors of the spheres are states with entropies greater than zero and at a maximum at the \( z \)-axis. In any evolution of state be it quantum mechanical or quantum thermodynamic, the \( \mathbf{r} \) vector processes around the \( z \)-axis with an angular frequency of \( \Omega_0 \) and because the system is isolated, the internal energy remains constant, while \( \mathbf{r} \) is at an angle of 0° to 180° with respect to the \( z \) axis.

Depicted in Figure 2.4a is what QM predicts, namely, that the thermodynamic state of the system, i.e., the vector \( \mathbf{r} \), must always touch the surface of the unit sphere and, thus, \( \mathbf{r} \) can only process around the \( z \)-axis on the surface of the sphere. The entropy as a result cannot increase. IQT by contrast predicts that even though the system is isolated, it can spontaneously relax to a state of maximum entropy. As shown in Figure 2.4b, this means that the end point of \( \mathbf{r} \) remains in contact with the shaded plane of constant energy as it spirals inward (relaxes and processes) toward the \( z \)-axis. At stable equilibrium, \( \mathbf{r} \) is co-directional with the \( z \) axis but is less than unit length. For the example shown in the figure, \( \mathbf{r} \) will be oriented downward at stable equilibrium.
The form of the IQT equation of motion (equation (2.8)) used to model this two-level system is given by (Beretta, 1985a)

\[
\frac{d\mathbf{r}}{dt} = \Omega_0 \mathbf{A} \times \mathbf{r} - \frac{1}{\tau} K(\mathbf{r})[\mathbf{r} - (\mathbf{A} \cdot \mathbf{r})\mathbf{A}]
\]

(2.39)

where \( \mathbf{A} \) is a unit norm, 3-vector of real scalars, \( \tau \) is the dissipative time constant, and

\[
K(\mathbf{r}) = \frac{f(\mathbf{r})}{1 - (\mathbf{A} \cdot \mathbf{r})^2}
\]

(2.40)

where

\[
f(\mathbf{r}) = \begin{cases} 
1 & \text{if } \mathbf{r} = 0 \\
\frac{1 - r^2}{2r} \ln \frac{1 + r}{1 - r} & \text{if } 0 < r < 1 \\
0 & \text{if } r = 1 
\end{cases}
\]

(2.41)

Beretta suggests a straightforward experiment involving the paramagnetic resonance properties of a spin-\( \frac{1}{2} \) particle that could be useful in verifying the hypothesis of spontaneous internal energy redistribution that is predicted by the IQT equation of motion for a two-level system. A beam of the particles is to be directed through a sinusoidally varying but spatially uniform magnetic field. The beam is very dilute so that the only interaction the particles have is with the external field and not with each other. The particles enter the field in a non-equilibrium state that corresponds to a relaxed state with respect to the field, evidently to prevent induced
changes to the state of the particles by the field. The energy change for each particle during its transit through the apparatus is small with the overall behavior of the particles being free of significant transient effects. Under these conditions, any relaxation by the particles toward equilibrium should mostly be due to internal dissipation within the particles themselves. The IQT equation of motion predicts that as a result, there should be noticeable asymmetries in both the real and imaginary parts of the susceptibility curve (also known as the absorption and dispersion curves in the terminology of magnetic-resonance experiments) as seen in Figure 2.5.

![Figure 2.5. Theoretical shapes for the real and imaginary susceptibility curves of magnetic resonance for a two-level spin system. The curve marked $\chi'$ is the real (absorption) part and the curve marked $\chi''$ is the imaginary (dispersion) part. The quantity $\gamma H_0$ is the Larmor ("natural") precession frequency of the particles due to $H_0$, a constant external magnetic field, $T_2$ is the relaxation time due to spin to spin interaction between individual particles and $\omega$ is the frequency of a weaker, modulated external magnetic field. Reprinted under fair use, from Pake and Estle 1973, W. A. Benjamin.](image)

taken from Pake and Estle (1973). In addition, the experiment, if conclusive, would verify the existence of quantum states that have entropy greater than zero and would help to determine a value for the time constant for the IQT equation of motion.

### 2.1.2.2 Resonance Fluorescence of a Two-Level System and the IQT Equation of Motion

In another 1985 paper, Beretta (1985b) uses IQT concepts and the IQT equation of motion to model the irreversible relaxation effects of a two-level system that is driven near resonance by a monochromatic laser beam. The phenomena studied are resonance fluorescence, absorption and stimulated emission. A comparison with a Quantum Electrodynamics (QED)
model for resonance fluorescence, which is, of course, based on a reversible evolution of state, is found in Kimble and Mandel (1977). For resonance fluorescence to occur, the system is driven by a laser at frequency equal or nearly equal to the energy gap between the two system energy eigenlevels. The impinging photons of the laser are absorbed by the atom causing electrons in the lower energy eigenlevel to jump to the higher level. After some time, the electrons fall back to the lower level and a photon is emitted in a random direction. The IQT equation of motion predicts a broadening not predicted by QED of the absorption and emission peaks because of dissipation effects caused by a redistribution of the internal energy of the system. Beretta (1985b) considers the effect to be strong enough to be detectable in a high resolution study. However, confirming experiments have yet to be performed.

Figure 2.6 shows the broadening of the absorption peak of the two-level system as predicted by IQT for varying strengths of the internal dissipation. The parameter $\delta$ is proportional to the relative magnitude of the dissipation and correlates with the time constant $\tau$ of the IQT dissipation operator. The time constant is a physical parameter dependent on the type of atom being tested. The symbol $\eta$ indicates the strength of the driving laser beam, while $\theta$ is a detuning parameter that indicates how closely the frequency of the laser light matches the natural resonance frequency of the system. The peaks in Figure 2.6a represent the system being driven

![Figure 2.6](image)

**Figure 2.6.** The broadening of absorption peaks as predicted by IQT and its equation of motion for a two-level system driven by a) a weak ($\eta=0.1$) laser beam and by b) a strong ($\eta=10$) laser beam (Beretta, 1985b). Used with permission, Nova Science Pub.
by a weak laser beam, while the peaks in Figure 2.6b correspond to the effects of a strong driving beam on the system. As is seen in the diagrams, the broadening effect due to internal dissipation ($\delta > 0$) is most pronounced in the weakly driven system with the greatest broadening corresponding to the largest internal dissipation. The QED prediction is that which corresponds to $\delta = 0$.

The effects of internal dissipation on the emission spectrum as predicted by IQT are shown in Figure 2.7 for various values of the dissipation strength $\delta$. The spectrum in Figure 2.7a represents a perfectly tuned system with a detuning value of $\theta = 0$ for the beam frequency. The spectrum in Figure 2.7b has a detuning value of $\theta = -10$. Both examples are strongly driven, with a $\eta$ value of 10 for the beam strength. The symbol $\nu$ indicates the breadth in the frequency of the emitted light. Again, the QED prediction is given by $\delta = 0$.

Asymmetry is seen when the driving frequency is slightly off resonance (i.e., in this case when $\theta = -10$). The IQT equation of motion indicates that the asymmetrical effect is even more pronounced than is expected with QED (i.e., for $\delta = 0$). Asymmetries for both absorption and stimulated emission have been observed in a number of experiments (Schuda et al. 1974; Wu et al., 1975; Hartig et al. 1976; Grove, Wu and Ezekiel, 1977; Cresser et al. 1982; Prentiss and Ezekiel, 1987; Toor and Zubairy, 1994) and have been attributed to the bandwidth of the driving laser (Kimble and Mandel, 1977), atomic recoil effects (Prentiss and Ezekiel, 1987) and resonant cavity losses (Toor and Zubairy, 1994). Beretta (1985b) asserts that the internal relaxation

![Figure 2.7. Broadening and enhanced asymmetry of the emission spectrum as predicted for a) a perfectly tuned ($\theta = 0$) and b) a detuned ($\theta = -10$) two-level system by QT and its equation of motion (Beretta, 1985b). Used with permission, Nova Science Pub.](image-url)
predicted by IQT should enhance the magnitude of the asymmetries caused by inelastic scattering strongly enough to be measured for experimental cases driven by broad bandwidth excitation.

2.1.2.3 Relaxation of a Rb System and the IQT Equation of Motion

Turning now to the work of Çubukçu (1993), his dissertation contains a number of topics that are of interest dealing with the foundations and applications of IQT including supporting experimental data. Çubukçu (1993, 2006) provides some examples of experiments that are deemed useful in verifying the predictions of IQT. The first is an experiment by Franzen (1959) that examines the spin lifetime of the single valence electron of a rubidium (Rb) atom. A rarified vapor of Rb in a glass vessel is subjected to an external magnetic field. The valence electrons are put into an excited spin state by means of a process called optical pumping. After a time, the pumping is turned off, and the electrons are allowed to relax. A chart showing the spin relaxation time versus vapor pressure is given in Figure 2.8.

According to QM, the electrons are thought to relax to the lower energy spin state due to collisions between the Rb atoms. The vessel has been coated with an organic substance, tetracontane, to reduce the speed of relaxation due to collisions with the container walls. However, if the relaxation were due to collisions, one would expect to see an inverse proportionality between the relaxation time and the vapor pressure. Figure 2.8 shows just a trend.
with an increase of the relaxation time as the vapor pressure decreases. However, at sufficiently low pressures, the trend plateaus, which is seen as evidence of the spontaneous relaxation predicted by IQT since the implication is that collisions play a much diminished role in the relaxation. In addition, when the Rb atoms are left in the dark, the relaxation to stable equilibrium continues, something which is not predicted by QM at all. It is, however, by IQT.

In the second experiment (Kukolich, 1967), Rb atoms mixed with a neon buffer gas are put into a non-equilibrium spin state via optical pumping in the same way as in the previous experiment. Instead of the pumping being turned off, the orientation of the magnetic field is changed suddenly. The intensity of the pumping light that is transmitted after the switch in orientation is used to indicate the occupation percentages of the relaxed and excited states. Figure 2.9 shows the results at two different time scales. The oscillations are predicted by QM, but the damping (i.e., dissipation) behavior is not. Kukolich attributes the attenuation to inhomogeneities in the external magnetic field without discussion of the details. Collisions of Rb atoms with the walls, each other and the electrode are also known to contribute to the spin decay. IQT predicts that spontaneous internal relaxation within the individual Rb atoms contributes to the damping effect.


Çubukçu models this second experiment by using a closed form solution of the Beretta equation (Beretta, 1985a) for a two-level spin system to predict the behavior of the relaxation. The amplitude $r$ of the solution is found to decay in time $t$ according to
\[ r(t) = \tanh \left( \frac{1}{2} \exp(-t/\tau) \log \frac{1+r(0)}{1-r(0)} \right) \]  \hspace{1cm} (2.42)

Both the oscillations and the damping are predicted with this model, agreeing qualitatively with the experimental results. However, a quantitative verification is lacking because in reality the valence electrons of Rb carry a spin of 2 instead of \( \frac{1}{2} \) so a five-level spin system should have been used to model the relaxation. Thus, the solution used by Çubukçu is only approximate yet it predicts what the Schrödinger (or von Neumann) equation cannot, i.e., the damping. Of interest for future work would be to numerically instead of analytically solve the IQT equation of motion for a five-level system to verify if the predictions agree quantitatively as well.

Finally, Çubukçu also suggests repeating the Kukolich experiment but in a vessel lined with tetracantane and without the buffer gas so as to remove any possible damping effects that could be attributable to the buffer gas. With the vapor pressure low enough, there is then stronger justification in treating each Rb atom as a separate one-atom system, which much simplifies the physical model, making it easier to isolate the spontaneous relaxation effect that IQT predicts.

2.2 Basic Developments in Quantum Thermodynamics (QT)

There are a number of methods by which QT attempts to deal with thermodynamic irreversibilities at the quantum scale. One of the more traditional is through what are known as “system-plus-reservoir” methods. For these, QMEs are commonly used to model the effects of quantum relaxation (Weiss, 2008; Blum, 1996; Gemmer, Michel and Mahler, 2004, 2009; Zurek, 1991; Zurek, 1993; Zurek and Paz, 1994) under the assumption that there is only a weak coupling between the system and reservoir. QMEs are used if the focus is on how the state function varies with time. A detailed development is found in Blum (1996) and for a broader overview see also Gemmer, Michel and Mahler, (2009). If, however, the focus is on how the measurement operators evolve, an equivalent treatment using Langevin equations (Weiss 2008) is employed. There have been a number of QMEs that have been proposed. The first was by Pauli (1928) with notable others such as those by Kossakowski (1972) and Lindblad (1976) as well as the so-called KSGL (Kossakowski, Sudharshan, Gorini, Lindblad) master equation (Liboff, 1979; Kossakowski, 1972; Ingarden and Kossakowski, 1975; Kossakowski, 1976).
Since correlations between the system and reservoir build up as a result of interactions according to standard QM unitary dynamics, the only way the QME formalism can work is to assume that there is a mechanism that removes the correlations at a much faster rate than the relaxation effects of interest being modeled. The mechanism that is used by QT is called the Markov approximation. The Markov approximation presumes that because the reservoir is so large and with so many degrees of freedom, any correlations with the system almost instantaneously diffuse away (Blum, 1996). The future state of the system is, thereby, said to depend only on its present state. This formalism describes a semi-group where trajectories can only be traced forward in time but not backward. What is touted as “irreversibility” amounts only to an irreversible loss of information.

Another assumption that is necessary for the QT formulation of quantum relaxation to work is called the secular approximation (Blum, 1996; Schaller and Brendes, 2008). The secular approximation assumes that the rapidly oscillating terms of the QT solution (i.e., the off-diagonal terms of the density operator or matrix) can be neglected. This approximation is only justified if the relaxation time of the interaction with the environment is much longer than the intrinsic relaxation time of the system. The oscillating terms can then be taken to average to a constant value. The secular approximation is associated with the technique often found in QT of “coarse-graining” system dynamics over time, a method which has the drawback of limiting the shortness of the time scale over which accurate solutions can be found. By contrast, because the equation of motion of IQT makes the claim that it is an exact solution to the relaxation problem, for isolated systems at least, no coarse-graining of this type is necessary. The oscillations remain fully represented in the solution with accuracy preserved no matter how short the time scale.

Once the approximations above have been applied, the QT solution to the quantum relaxation problem leads to master equations similar to the Pauli master equation (Pauli 1928; Blum, 1996) or the more general KSGL master equation. The KSGL equation of motion is expressed in operator format as

\[
\frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] + \frac{1}{2}\sum_j \left(2V_j^+ \rho V_j - \{V_j V_j^+, \rho\}\right)
\]

(2.43)

where the \(V_j\) and \(V_j^+\), the Hermitian adjoint of \(V_j\) represent creation, annihilation, or transition operators, \(\rho\) is the state operator, and \(H\) is the Hamiltonian operator. Its similarity in appearance to the IQT equation of motion is notable, but the dissipation mechanism that is
employed is fundamentally different in that it is not intrinsic and spontaneous but dependent on interactions with the environment. Under suitable conditions as noted in Beretta (2009a) and Beretta (1981), equation (2.43) reduces to the famous Pauli master equation written in operator form as

\[
\frac{d\rho_{mm}(t)}{dt} = \sum_{n \neq m} \rho_{nn}(t) W_{mn} - \rho_{mm}(t) \sum_{n \neq m} W_{nm}
\] (2.44)

This equation relates how the probability of finding the system in energy eigenlevel \( m \) changes in time depending on the rate of transitions to and from the given energy eigenlevel. The transitions require interactions with a reservoir. However, only the diagonal terms of the density matrix i.e., \( \rho_{mm} \) and \( \rho_{nn} \), are considered. The first term on the right hand side of the equation is the “loss” term. With the transition rate factor \( W_{mn} \), it gives the total probability that the system makes a transition from energy eigenlevel \( m \) to some other energy eigenlevel. The second term on the right hand side is the “gain” term and together with the summation of the rate factor \( W_{nm} \) gives the collective probability that the system makes a transition from all other energy eigenlevels to energy eigenlevel \( m \). Equations (2.43) and (2.44) have played a prominent role in applications to many problems in physics, chemical kinetics, and biology (Haken, 1978).

Despite all the clever mathematical work and considerable success that theories like QT have had, a problem with which these approaches must contend is the inconsistency of the modeling of irreversible and nonlinear processes with dynamics that are reversible and linear, that is, the so-called Loschmidt Paradox. An insightful criticism taken from the point of view of IQT is found in Beretta (2009).

A related and more serious problem, however, is the violation of the Second law that is inherent within QT and other theories derived from reversible equations. A system and reservoir that are not in mutual stable equilibrium have the potential of producing work through the harnessing of the gradients of temperature, pressure, etc. that exist between them. Once mutual stable equilibrium is established, the ability to do work via gradients, i.e., the adiabatic availability, is lost. The overall energy remains the same but the potential for doing work has diminished. Nevertheless, QT asserts that the entropy of the system plus reservoir as a whole remains at all times constant despite any diffusions of correlations across boundaries. As a result, a fundamental conclusion that can be made about the QT point of view is that the Second
Law of thermodynamics does not exist. As a consequence, there is the possibility, at the microscopic level at least, that work could be extracted directly from the internal energy of a reservoir at stable equilibrium, leading to the prospect of a perpetual motion machine of the second kind, something that has never been observed. The theory of IQT contradicts these notions at the fundamental, microscopic level. IQT incorporates the Second Law through the idea of energy spreading among available energy eigenlevels, which enables IQT to simultaneously remain consistent with the Second Law as well as Quantum Mechanics.

2.3 Quantization Methods

Alternative theories for dealing with quantum dissipative systems include the development of non-linear Schrödinger equations (NLSEs) and the related field of using explicitly time dependent, dissipative Lagrangians and Hamiltonians (DL) to produce a Schrödinger equation that includes dissipative effects. The first ideas towards a NLSE were put forward by Schrödinger (1926), who, as in most subsequent models, inserted logarithmic terms to produce dissipation. Other NLSEs by, for example, Kostin (1972) and Yasue (1978) have been criticized because their theories violate the superposition principle. The result is that two separate solutions to an NLSE do not necessarily sum to form an additional solution. The version presented by Schuch (1997) claims to resolve these difficulties. It takes the form,

\[i\hbar \frac{\partial}{\partial t} \Psi = \left( H_L + \gamma \frac{\hbar}{i} \left( \ln \Psi - \ln \langle \Psi \rangle \right) \right) \Psi \]

(2.45)

where \( \Psi \) is the wave or state function; \( H_L \) the linear, conservative Hamiltonian; and \( \gamma \) the coefficient of viscous friction. The logarithmic functions of \( \Psi \) model the dissipation.

The dissipative Lagrangian (DL) approach started with Caldirola (1941) and Kanai (1948). The version by Dekker (1981) was able to reproduce the Fokker–Planck equation under certain circumstances. More recent contributors include Schuch (1990) and Smith (2010). Examples, (Schuch, 1990), of a dissipative Lagrangian \( L \) and Hamiltonian \( H \) for a damped harmonic oscillator are

\[ L(q, \dot{q}, t) = \frac{m}{2} \left( \dot{q}^2 + \gamma \dot{q} \right) + \frac{\gamma^2}{2} q^2 - \omega^2 q^2 \exp(\gamma t) \]

(2.46)
\[ H(q, p, t) = \frac{m}{2} \left( \frac{p^2}{m^2} + \frac{\gamma}{m} p q + \frac{\gamma^2}{2} q^2 + \omega^2 q^2 \right) \exp(\gamma t) \]  

where \( q \), \( \dot{q} \), and \( p \) are the generalized coordinates, velocities, and momenta, respectively, and \( m \), \( \gamma \) and \( \omega \) the mass, frictional coefficient, and angular frequency. When the variation of equation (2.46) is determined from the variational principle using the Euler-Lagrange equation, it is seen that the expected classical equation of motion is produced. It is also seen that the Hamiltonian (equation (2.46)) is a constant of the motion. The task which remains is to use the Hamiltonian as a starting point for canonical quantization.

The DL approach has also been criticized, but in this case for violating the Heisenberg uncertainty principle, where the formulations imply that the fundamental limit \( h \) shrinks exponentially with time for dissipative systems. Schuch (1997) was able resolve the violation by arguing that the non-unitary transformations that are used must also apply to the wave function as well as the operators. In addition, Schuch also apparently shows that the NLSE and DL techniques are intimately related to one another and shows that equation (2.47) obeys both the superposition as well as the Heisenberg uncertainty principle.

The NSLE and DL techniques, like the IQT equation of motion, are attempts to modify the Schrödinger equation in order to reproduce entropic effects. No statistical ansatz is used. There are no theoretical inconsistencies due to the definitions of state and ensemble nor an apparent irreversibility paradox. However, the two points of view differ in important ways. The NSLE and DL methods model in essence a many-body system that tries to predict the quantum behavior of a few particles of interest interacting with another group of particles that serve only as a dissipative medium. For simplicity, the dissipation is expressed phenomenologically, usually as a type of viscous retarding force. As a result, the internal friction alters the energy eigenlevel structure for the system, which is not the case with systems currently modeled using the IQT equation of motion. With the NLSE and DL techniques, the entropy may be inferred but is not explicitly expressed. The state of the system is often represented by state vectors (wave functions) rather than density operators.

Çubukçu (1993) makes a strong criticism that questions the validity of NLSEs in general by demonstrating the non-uniqueness of their evolutions when their corresponding density operators are calculated (Çubukçu, 1993). A less direct connection to density operators and QT
has also been made via Wigner distributions (Dekker, 1981). Although the focus of considerable attention over a span of some eighty years, NLSE and DL techniques have found very few applications to physical systems due to the above mentioned quantum mechanical inconsistencies. Since the ostensibly effective rationalization by Schuch (1997) regarding QM, Schuch and Moshinsky (2003) have offered a model of damped cyclotron radiation. A detailed overview of dissipative quantization schemes is given by Razavy (2005).

2.4 Brief Discussion of Pertinent Carbon Nanotube Literature

The bulk of the information regarding the physical arrangement of molecules with regards to the storage of hydrogen on carbon nanotubes has come from simulations rather than direct experiments. The two most common methods of simulation are classical: Monte Carlo simulations (MC) and molecular dynamics (MD). There is a considerable literature concerning the simulation of the hydrogen storage problem, e.g, Lee et al., (2000), Lee and Lee (2000), Cabria, Lopez and Alonso (2006), Han and Lee (2004), Rzepka, Lamp and Casa-Lillo (1998), Wang and Johnson (1999), Luo and Lloyd (2009), Gu et al. (2001), Zheng, Wang and Cheng, (2004), Meregalli and Parrinello (2002), Banerjee (2008), Knippenberg, Stuart and Cheng (2008), Cheng et al. (2005), Maruyama and Kimura (2000), Dodziuk and Dolgonos (2002). Seemingly little of it is in a form that could readily be compared to results achieved by a IQT simulation of hydrogen stored on a carbon nanotube as a function of time from an initial non-equilibrium state. An MD simulation of hydrogen storage starting with non-equilibrium conditions could readily be conducted but no such study was found during this doctoral work. The results of every study in the literature examined to date, is concerned with storage performance at stable equilibrium.

Data for stable equilibrium conditions can be a useful benchmark in comparisons with a IQT simulation, especially if it is in the form of a quantitative representation of hydrogen density profiles as a function of distance from the nanotube. Relatively little of the literature presents the results in this form, however. Some information can be useful for other reasons. Banerjee (2008) stresses the importance of accurately modeling the Coulombic potential around the simulated molecules in order to achieve the most quantitatively accurate dynamic results. The simplest type of potential that has been utilized for modeling hydrogen adsorption on carbon nanotubes is the Lennard-Jones (L-J) potential that has been parametrically adjusted to represent
the interactions between hydrogen and carbon and hydrogen and hydrogen. Due to its ease of implementation and reasonable accuracy, the L-J potential was used for the study of hydrogen-carbon nanotube interactions featured in this dissertation. If the utmost in accuracy is desired more complicated potentials such as the Crowel-Brown potential or Silvera-Goldman potentials are available. Highlighted below are some initial findings that may be useful for comparing with the IQT simulations of this doctoral research.

Rzepka, Lamp, and Casa-Lillo (1998) studied the amount of hydrogen adsorption by van der Walls forces using MC simulations and experimental data. Pressures ranged from 0-40 MPa and temperatures from 77 K to over 400 K with the greatest amount of storage occurring near 10 MPa and 77 K. Colder conditions and higher pressures lead to better hydrogen storage. The amount of storage on graphene sheets and carbon nanotubes were studied. Their paper presents spatial density profiles for graphene sheets indicating storage density peaks occurring about 4 Å from the center of carbon atoms. Their results can at least be qualitatively compared to simulations using IQT and its equation of motion. Figure 2.10 shows how storage density varies with the separation distance between the graphene sheets.

![Graph showing variation of hydrogen density between two graphene sheets at various distances for T = 300 K and p = 10 MPa](image)

Figure 2.11. Density profiles inside clusters of a) the (18, 18) carbon nano-tubes and b) the (9, 9) carbon nanotubes at 77 K and 50 atm (Wang and Johnson, 1999). The radii of the (18, 18) and (9, 9) nanotubes are 12.21 Å and 6.10 Å respectively. Used with permission, Am. Inst. Physics.

Figure 2.12. Density profile for hydrogen adsorbed on the internal and external surfaces of an isolated (9, 9) single-walled nanotube (SWNT) at 77 K and 50 atm (Wang and Johnson, 1999). The tube radius is 6.10 Å. Used with permission, Am. Inst. Physics.

Wang and Johnson (1999) show storage density profiles with corresponding carbon nanotube specifications that could be used for comparison with IQT predictions. They used a grand canonical MC simulation that included quantum effects by means of implementing a path
integral formalism. Quantum effects were seen especially in the interstices of the carbon mesh up to 298 K. A Crowel-Brown potential was employed to model the hydrogen carbon interactions while a Silvera-Goldman potential was used for the hydrogen-hydrogen interactions.

Figure 2.11 shows the density profiles inside the tubes for two different diameters. Figure 2.12 gives an idea of the density profile on the outside of the tube as well. The temperature of 77 K looks to be nearer to the range of possible temperatures accessible with current IQT simulations. Similar density profile results are found in studies by Luo and Lloyd (2009) and Gu et al. (2001).
Chapter 3 - Theoretical Foundations

3.1 IQT Basics: Systems, Properties, States, Processes and Interactions

In addition to the postulates, the strength of the arguments that IQT makes is in no small part due to a strict set definitions of the basic thermodynamic concepts on which IQT is based. Such definitions are useful for scientific endeavors in general apart from thermodynamics and help to prevent unneeded compromises, circular arguments or unnecessary restrictions that may lead to ambiguities or inconsistencies in scientific discussions. Some of the most basic concepts that need to be defined for a clear thermodynamic discussion are the ideas of system, properties, states, processes and interactions. The following is based on Gyftopoulos and Beretta (1991, 2005) and serves as a basis for subsequent developments for our research.

**System:** A well defined system is a collection of constituents determined by the following specifications.

1. The type and range of values of the amount of each constituent $\tilde{n} = \{n_1, \ldots, n_r\}$. For example the number of molecules could be specified or a range of mass for each constituent.
2. The type and range of values of the parameters, $\tilde{\beta} = \{\beta_1, \ldots, \beta_s\}$ that fully characterize the external forces exerted on the constituents, such as the volume and geometrical shape of a container enclosing the system or the strength of an applied electrostatic field.
3. The internal forces between the constituents such as the forces between two water molecules or internal partitions that separate constituents in one region of the system from constituents in another region.
4. Internal constraints, for example, that require the volume or internal energy of a system to remain constant or conditions that allow certain chemical reactions to be active while other reactions remain inactive.

In practice, the system definition also includes defining the boundaries enclosing the system, be they physical or imaginary. Accurate results due to interactions or processes depend greatly on keeping the system boundaries consistent throughout a process. Furthermore, the idea that a
system can even be determined requires that the object under study be *separable* from the environment (Gyftopoulos and Beretta 1991, 2005). Separability requires that the external forces that affect the object of study from the environment not depend on the coordinates of the constituents in the environment. For example, one atom of a hydrogen molecule cannot be considered a system because the external forces it experiences depend on the position of the other atom. Both atoms of the molecule must be included in order to define a system that is separable from the environment.

**Properties**: A property is an attribute of a system that can be evaluated or measured at one given instant of time. Properties have a numerical value. Quantities that take more than one instant of time to evaluate such as the distance a molecule travels over a given interval of time are not considered properties. For the state of the system to be definable, all properties must be able to be evaluated at the same instant of time. Properties may be independent of one another or can be functionally related or statistically correlated. Common properties of a system include energy, temperature, entropy, available energy, pressure, etc.

**States**: For a given system, the values of the amounts of all the constituents, the values of all the parameters and the values of a complete set of independent properties are all that can be known about a system at a given instant of time and as such constitute a complete characterization of the system at that given instant of time. Such a characterization is defined as the state of the system. Two systems are said to be *uncorrelated* if the state of the composite of the two systems depends only on the original states of two systems and nothing else. Otherwise the two systems are correlated. A relation that describes the time evolution of the state of a system is called an equation of motion. The equation in postulate 5, the dynamic postulate formulated by Beretta, is the equation of motion for IQT systems that governs how thermodynamic states change over time.

**Processes**: For a process to be specified, it is necessary only that the beginning and end states are able to be defined as well as the modes of interaction. A process that involves no modes of interaction with the environment is called a spontaneous process. A reversible process can be performed in at least one way such that both the system and environment can restored to their original states. Any process that is not reversible is called an irreversible process. A spontaneous process is an example of an irreversible process. During a process the constituents
of a system may not always be separable from the environment or other systems. The system, state of the system, along with an equation of motion may not always be definable during the course of the process.

**Modes of Interaction:** During the course of a change of state for a system, modes of interaction are active if the changes take place because of influences from the environment or other systems. Each mode of interaction is characterized by the type of flow that crosses the system boundary. A work interaction involves an inflow or outflow of energy only with respect to the system boundary. For a heat interaction, energy and entropy cross the boundary. A mass interaction involves the exchange of energy, entropy and mass across the system boundary. An idealized work interaction involving a frictionless deformation of the system boundary can be considered is an example of a reversible process. Heat and mass interactions are normally considered to be irreversible because additional entropy is almost always generated due to the existence of finite temperature and concentration gradients. However, in the limit, for example, as the temperature gradient between the system and the environment becomes infinitesimally small, a heat interaction becomes reversible.

### 3.2 Mathematical Preliminaries: Operators, State Vectors, Unitary Transformations

Much of the IQT formalism has its basis rooted in the concepts of density operators and the mathematical operations that go along with them. The concepts involved in the following discussion are a summary of what can be found in texts such as Messiah (1976), Blum (1996) and McMahon (2006).

In physics, an operator is a mathematical instruction that acts on the state function or state matrix of the system. Some operators change the state function. Operators that are associated with the measurement of an observable quantity leave the state function unchanged but multiplied by an eigenvalue of the operator. The eigenvalue represents a result of the measurement and is a real number. Examples of observables include energy, momentum, spin, particle position and angular momentum. IQT asserts that entropy should also be added to the list. Each observable is represented by its own distinct operator which is often represented as a square matrix. A measurement returns a value for the observable that is one of the eigenvalues of the matrix.
Operators that represent measurable observables have the following properties:

1. Operators are Hermitian, that is if $A$ is Hermitian it is equal to the transpose of its complex conjugate: $A = A^\dagger$.

2. The diagonal values of its matrix representation are real.

An example of a Hermitian matrix is

$$\begin{bmatrix}
1 & 3+i \\
3-i & 2
\end{bmatrix}$$

(3.1)

The off-diagonal elements do not have to necessarily be complex.

The state operator, also called a density operator is denoted as $\rho$ and is an example of a Hermitian matrix. The state operator contains all the information that can be known about the system.

Any Hermitian matrix can be diagonalized via the application of the proper unitary matrices. A diagonal matrix has real entries along the diagonal and is zero elsewhere. A unitary matrix $U$ is such that the inverse of $U$ is its complex conjugate:

$$U^{-1} = U^*$$

(3.2)

Diagonalization by means of a unitary matrix is an example of a similarity transformation where the eigenvalues of the matrix are preserved after the transformation. Diagonalized matrices are considered to be symmetric and are a subset of Hermitian matrices.

A set of matrices $\{A_1, \ldots, A_n\}$ are said to be simultaneously diagonalizable if there exists a single invertible (unitary) matrix $U$ such that $U^{-1}A_{(i)}U$ is a diagonal matrix for every member $A_{(i)}$ in the set $\{A\}$. The following theorem characterizes simultaneously diagonalizable matrices: A set of diagonalizable matrices commutes if and only if the set is simultaneously diagonalizable. All eigenvalues of a Hermitian matrix are real and the eigenvectors with distinct eigenvalues are orthogonal.

Given that the vectors $|a_i\rangle \ (i = 1, \ldots, n)$ form a set of discrete basis vectors, an operator $A$ can be represented as a matrix with respect to the basis. The elements of the matrix are

$$A_{ij} = \langle a_i | A | a_j \rangle = \sum_{i,j=1}^{n} A_{ij} |a_i\rangle \langle a_j|$$

(3.3)

The expression $|a_i\rangle \langle a_j|$ is an outer product between a column and row basis vector, e.g.,
with 1’s in the $i^{th}$ and $j^{th}$ positions respectively. The result forms an $n \times n$ matrix and so is itself an operator. As an example, let

$$|a_i\rangle \langle a_j| = \begin{bmatrix} 0 & \cdots & 0 & 1 & 0 & \cdots & 0 \end{bmatrix}$$

(3.4)

and

$$|a_i\rangle = \begin{bmatrix} 0 \\ 0 \\ \vdots \\ 1 \\ 0 \\ \vdots \\ 0 \\ \end{bmatrix}$$

$$|a_j\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ 0 \\ \end{bmatrix}$$

(3.5 a,b)

The outer product $|a_i\rangle \langle a_j|$ is then

$$\begin{bmatrix} 0 \\ 1 \\ \end{bmatrix} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}$$

(3.6)

The matrix representation of operator $A$ as given by equation (3.3) is

$$A = \begin{bmatrix} \langle a_1|A|a_1\rangle & \langle a_1|A|a_2\rangle & \cdots & \langle a_1|A|a_n\rangle \\ \langle a_2|A|a_1\rangle & \cdots & \cdots & \langle a_2|A|a_n\rangle \\ \vdots & \cdots & \cdots & \vdots \\ \langle a_n|A|a_1\rangle & \cdots & \cdots & \langle a_n|A|a_n\rangle \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & \cdots & A_{1n} \\ A_{21} & \cdots & \cdots & \vdots \\ \vdots & \cdots & \cdots & \vdots \\ A_{n1} & \cdots & \cdots & A_{nn} \end{bmatrix}$$

(3.7)

Another way to express operator $A$ is in terms of its eigenvectors. When $A$ operates on eigenvector $|u_i\rangle$, the result is

$$A|u_i\rangle = \lambda_i |u_i\rangle$$

(3.8)

where the eigenvector is returned, multiplied by its eigenvalue $\lambda_i$. The operator $A$ with respect to its eigenvector basis is then,

$$A = \sum_{i,j=1}^{n} \lambda_i |u_i\rangle \langle u_i|$$

(3.9)

The operator $A$ as a result of equation (3.9) can then be represented as a matrix such that

$$A = \begin{bmatrix} \langle u_1|A|u_1\rangle \\ \vdots \\ \langle u_n|A|u_n\rangle \end{bmatrix} = \begin{bmatrix} 0 \\ \vdots \\ 0 \end{bmatrix}$$

(3.10)

In contrast to equation (3.7), an operator represented with respect to its eigenvectors is diagonal.

The expression,

$$P_i \equiv |u_i\rangle \langle u_i|$$

(3.11)
is the projection operator for the \( i^{th} \) eigenstate. A projection operator takes any state function \(|\Psi\rangle\) and projects it onto vector \(|u_i\rangle\), in essence indicating the amount of \(|u_i\rangle\) that is contained in the state \(|\Psi\rangle\).

For example let \( \Psi = \alpha |0\rangle + \beta |1\rangle \), where \(|0\rangle\) and \(|1\rangle\) are orthonormal basis vectors and \( P_0 \) is the projection operator onto eigenvector \(|0\rangle\), then

\[
P_0 |\Psi\rangle = |0\rangle \langle 0 |\Psi\rangle = (|0\rangle \langle 0 |) (\alpha |0\rangle + \beta |1\rangle) = \alpha |0\rangle \langle 0 |0\rangle + \beta |0\rangle \langle 1 |1\rangle = \alpha |0\rangle
\]

(3.12)

Since the basis is orthogonal, \(|0 |1\rangle = 0\) and \(|0 |0\rangle = 1\).

Other properties of projection operators include

\[
\sum_i P_i = \sum_i |u_i\rangle \langle u_i | = I,
\]

(3.13)

\[
P_i P_j = |u_i\rangle \langle u_i | u_j \rangle \langle u_j | = |u_i\rangle \langle u_j | \delta_{ij}
\]

(3.14)

If \( i \neq j \) then \( P_i P_j = 0 \) and for \( i = j \) it is easily shown that

\[
P_i P_i = P_i^2 = P_i
\]

(3.15)

The density operator \( \rho \) for a pure quantum state \(|\Psi\rangle\) where entropy is zero is defined as the projector,

\[
\rho = |\Psi\rangle \langle \Psi |
\]

(3.16)

A pure state wave function \(|\Psi\rangle\) expanded into \( n \) basis vectors, has \( n \) eigenvalues for its density matrix with \( \rho \) consisting of a 1 in the diagonal and the remaining \( n-1 \) values being zero.

The density operator for mixed, or impure states can be represented as a linear combination of pure states

\[
\rho = \sum_{i=1}^{n} p_i |\Psi_i\rangle \langle \Psi_i |
\]

(3.17)

in much the same way that a state function, \(|\Psi\rangle\), can be decomposed into a sum of energy eigenstates. The \( p_i \) are the eigenvalues of \( \rho \), which must sum to unity. It should be noted that in both IQT and QT the density operator \( \rho \) represents the state of the system and not the individual pure states. However, in QSM the pure states do represent the various “states” that the system may have. In QSM the system does not possess a single definite state.

For an impure state none of the eigenvalues of \( \rho \) are equal to 1, which results in the system having an entropy greater than zero. Additional properties of the density operator \( \rho \) include
1) Hermiticity: \[ \rho = \rho^+ \] (3.18)

2) Trace normalization: \[ \text{Tr}(\rho) = 1 \] (3.19)

3) Idempotence for pure states: \[ \rho^2 = \rho, \quad \text{Tr}(\rho^2) = 1 \] (3.20)

4) Non-idempotence for mixed states \[ \rho^2 \neq \rho, \quad \text{Tr}(\rho^2) < 1 \] (3.21)

5) Range of the eigenvalues for \( \rho \) \[ 0 \leq \lambda_i \leq 1 \] (3.22)

Whether the state of a system is pure or not pure, the density matrix can be used to make all of the physical predictions of the state that are possible within the framework of QM and IQT.

The expectation value for observable \( A \) can be expressed as

\[ \langle A \rangle = \text{Tr}(\rho A) \] (3.23)

which using equation (3.16) is equivalent to

\[ \langle A \rangle = \text{Tr}(\langle \psi | A | \psi \rangle) = \text{Tr}(\langle \langle \psi | A | \psi \rangle) = \langle \langle \psi | A | \psi \rangle \] (3.24)

The expression in the trace is just a scalar so the trace operation vanishes. For equation (3.24) to have physical meaning the operators \( \rho \) and \( A \) are represented in terms of the same set of basis vectors.

Common operators besides the state operator \( \rho \) that are seen in QM and IQT are the Hamiltonian operator \( H \), which describes observations having to with the energy of the system, the entropy operator \( S \), which describes the distributions of measurements and \( x \) an operator which governs observations of particle position.

For specific measurements whose outcomes are independent of one another, projection operators are useful. The results of a measurement that yields the value \( \lambda_m \) can be represented by the projection operator

\[ P_m = |m\rangle \langle m| \] (3.25)

where \( |m\rangle \) represents the \( m^{th} \) eigenvector for the system. The probability of obtaining the eigenvalue \( \lambda_m \) as a measurement result is then

\[ \text{Prob}(\lambda_m) = \text{Tr}(\rho P_m) = \text{Tr}(\rho|m\rangle \langle m|) = \langle m|\rho|m \rangle \] (3.26)

The expressions in (3.26) are equivalent to the Born Rule (e.g., Liboff, 1998) for determining the probability of a measurement, i.e.,

\[ \text{Prob}(\lambda_m) = |\langle m|\psi \rangle|^2 \] (3.27)
A discussion about the commutation of operators is in order since this concept is often encountered. Two operators $A$ and $B$ are said to commute if the order in which they are applied does not matter, that is, if

$$AB = BA$$

or equivalently if,

$$AB - BA = 0$$

A common way of expressing (3.28) and (3.29) is with the Poisson bracket also known as a “commutator”

$$[A, B] = 0$$

Operators in the context of physics are described by square matrices and it can be shown that two operators commute if the matrices that represent them can be simultaneously diagonalized via identical unitary operations. Specifically, any square matrix $A$ can be diagonalized by using the following unitary transformation,

$$A_{\text{diagonal}} = U^{-1}AU$$

where $U$ is a matrix whose columns are the eigenvectors of $A$ while $U^{-1}$ is the matrix inverse of $U$. Two operators $A$ and $B$ commute if the same matrices $U$ and $U^{-1}$ that diagonalize $A$ will also diagonalize $B$, the implication being that $A$ and $B$ must have the same eigenvectors.

In IQT as in QM it is seen that sometimes operators commute and sometimes they do not. Operators that are functions of one another always commute. The Hamiltonian and momentum operators always commute since the Hamiltonian is related to the square of the momentum. The state operator $\rho$ and the entropy operator $S$ always commute since $S$ is proportional to the natural logarithm of the state operator. The operators for momentum and position never commute, which gives rise to the famous momentum-position Heisenberg uncertainty principle. For the state operator and the Hamiltonian however, it is the evolution of the trajectory of the system as it moves to stable equilibrium that determines whether $\rho$ and $H$ commute with one another.

For convenience, the Hamiltonian operator in IQT is chosen to be diagonal, while the state operator $\rho$, which is expressed in the basis of the Hamiltonian, may not be diagonal. The presence of non-zero off-diagonal elements in $\rho$ indicates the extent to which the system can exhibit quantum interference effects, also known as coherence or correlations. For a pure state, $\rho$ has off diagonal terms for which the relation $\rho^2 = \rho$ holds. Mixed states may also have off-
diagonal elements, but $\rho^2 \neq \rho$ and $\text{Tr}(\rho^2) < 1$. The off-diagonal terms of $\rho$ indicate that the density operator and the Hamiltonian do not commute, that is,

$$[\rho, H] = \rho H - H \rho \neq 0$$  \hfill (3.32)

The basis of $\rho$ and $H$ are the same but the set of eigenvectors for each differ.

In the case where the off-diagonal elements for both the density matrix and the Hamiltonian are all zero, the $\rho$ operator is simultaneously diagonal with $H$. The set of eigenvectors for $\rho$ and $H$ are identical and the operators $\rho$ and $H$ commute. The system is not in a pure state and no quantum interference effects are possible since $\rho$ has no off-diagonal terms. However, the system may or may not be in stable equilibrium. IQT indicates that for stable equilibrium states, $\rho$ is also diagonal and commutes with the Hamiltonian. Quantum coherence is zero. However, in addition, the eigenvalues for $\rho$ are such that the entropy for the system is maximized.

The IQT equation of motion predicts that over time the entropy for an isolated system in a non-equilibrium state will spontaneously increase. Off-diagonal terms will vanish and $\rho$ will converge to a matrix having only diagonal terms and maximal entropy at stable equilibrium. Valid starting points for the thermodynamic evolution for a state of such a system are mixed states. Any $\rho$ with or without diagonal terms is acceptable as long as it is not already at equilibrium (i.e. metastable, unstable or stable). However, it should be noted that elements of $\rho$ which initially are exactly zero do not change with time and can do so only if perturbed slightly.

The calculation of $\rho$ for a pure state is shown in the following. A state vector can be expanded in terms of its basis vectors $|u_i\rangle$ as

$$|\Psi\rangle = c_1 |u_1\rangle + c_2 |u_2\rangle + \ldots + c_n |u_n\rangle$$  \hfill (3.33)

Here the $|u_i\rangle$'s are eigenvectors of the Hamiltonian but not of $\rho$. The latter is expressed as

$$\rho = |\Psi\rangle \langle \Psi | = \sum_{i=1}^{n} |c_i|^2 |u_i\rangle \langle u_i| + \sum_{i \neq j} c_i c_j^* |u_i\rangle \langle u_j|$$  \hfill (3.34)

The elements of $\rho$ are found using equation (3.3). The first summation of equation (3.34) has terms only along the diagonal, i.e.,

$$|c_i|^2 = \langle u_i | \rho | u_i \rangle$$  \hfill (3.35)

For the second summation, the off diagonal terms are given by
\[ c_i c_j^* = \langle u_i | \rho | u_j \rangle \]  

(3.36)

Since the coefficients, the \( c_i \) and \( c_j \), are in general complex they can be written in the form

\[ z = re^{i\phi} \]  

(3.37)

where \( z = x + iy, \quad r = \sqrt{x^2 + y^2} \) and \( \phi = \arctan(iy/x) \). The phase \( \phi \) of each coefficient is related to the eigenenergies by

\[ \phi_j = -\frac{E_j}{\hbar} \]  

(3.38)

where \( E_j \) is the eigenenergy for the \( j^{th} \) eigenvector. Thus,

\[ c_j = |c_j| e^{-iE_j t/\hbar} \]  

(3.39)

and

\[ c_i c_j^* = \langle u_i | \rho | u_j \rangle = |c_i| |c_j| e^{-i(E_i - E_j)t/\hbar} \]  

(3.40)

The following is an example of the calculation of the density operator for a pure state. Let

\[ |\Psi\rangle = \sum_i c_i |u_i\rangle = \frac{3}{\sqrt{25}} |u_1\rangle + \frac{4}{\sqrt{25}} |u_2\rangle \]  

(3.41)

The density operator is then

\[ \rho = |\Psi\rangle \langle \Psi | \]

\[ = \left( \frac{3}{\sqrt{25}} |u_1\rangle + \frac{4}{\sqrt{25}} |u_2\rangle \right) \left( \frac{3}{\sqrt{25}} \langle u_1 | + \frac{4}{\sqrt{25}} \langle u_2 | \right) \]

\[ = \frac{9}{25} |u_1\rangle \langle u_1 | + \frac{12}{25} |u_1\rangle \langle u_2 | + \frac{12}{25} |u_2\rangle \langle u_1 | + \frac{16}{25} |u_2\rangle \langle u_2 | \]

\[ = \begin{bmatrix} \frac{9}{25} & \frac{12}{25} e^{i(E_2 - E_1) t} \\ \frac{12}{25} e^{-i(E_2 - E_1) t} & \frac{16}{25} \end{bmatrix} \]  

(3.42)

It is readily shown that \( \rho^2 = \rho \) and \( \text{Tr}(\rho^2) = 1 \) as is expected for a pure state. The \( \rho \) matrix is also non-invertible, since \( \det(\rho) = 0 \).

The expectation value for the energy is \( \langle E \rangle = \text{Tr}(\rho H) \)
(3.43) \[ \langle E \rangle = \text{Tr} \left[ \begin{pmatrix} \frac{9}{25} & \frac{12}{25} e^{i\frac{\hbar}{\epsilon}(E_2-E_1)t} \\ \frac{12}{25} e^{-i\frac{\hbar}{\epsilon}(E_2-E_1)t} & \frac{16}{25} \end{pmatrix} \right] = \text{Tr} \left( \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix} \right) = \text{Tr} \left( \begin{pmatrix} \frac{9}{25}E_1 & \frac{12}{25} e^{i\frac{\hbar}{\epsilon}(E_2-E_1)t} \\ \frac{12}{25} e^{-i\frac{\hbar}{\epsilon}(E_2-E_1)t} & \frac{16}{25}E_2 \end{pmatrix} \right) \]

\[ = \frac{9}{25}E_1 + \frac{16}{25}E_2 \] 

The expectation value of the entropy for the system is given by
\[ \langle S \rangle = \text{Tr}(\rho S) = -k \text{Tr}(\rho \ln(\rho)) \quad (3.44) \]

where \(-k \ln(\rho)\) is \(S\), the operator for entropy.

It is important to note that the operator \(\ln(\rho)\) is the natural logarithm function for the matrix itself and is not in general the log of each of the elements of the matrix, unless the matrix is diagonal. Since operators such as \(\rho\) are associated with physical quantities, they can be made to be diagonal with a suitable unitary transformation. This property can be used to find \(\ln(\rho)\). A diagonal matrix using the eigenvalues of \(\rho\) is created. The function of a diagonal matrix is then just the function applied to the diagonal members of the matrix:
\[ \ln(\rho_{\text{diag}}) = \begin{bmatrix} \ln(\lambda_1) & 0 & 0 & \cdots \\ 0 & \ln(\lambda_2) & 0 & \cdots \\ \vdots & \vdots & \ddots & \ddots \end{bmatrix} \quad (3.45) \]

The diagonal \(\ln(\rho)\) matrix can then if necessary be transformed back to the original non-diagonal basis.

To non-diagonalize \(\rho\), the normalized eigenvectors of the original non-diagonal \(\rho\) matrix are used to form the columns of a transformation matrix \(U\) and applied according to the unitary transformation,
\[ \ln(\rho_{\text{non-diag}}) = U^{-1} \ln(\rho_{\text{diag}}) U \quad (3.46) \]

If subsequent calculations do not require an explicit non-diagonalized form of \(\ln(\rho)\), the expectation value of the system entropy \(\langle S \rangle\) can be found directly from the eigenvalues of the \(\rho\) matrix, i.e.,
\[ \langle S \rangle = -k \sum_{i=1}^{n} \lambda_i \ln \lambda_i \quad (3.47) \]
where $\lambda_i$ are the eigenvalues of $\rho$. By using equation (3.46), one can also avoid the problem of dealing with a density matrix that is non-invertible, which occurs when the system is in a pure state as is true for our example here.

The eigenvalues for $\rho$ are found by solving the characteristic equation, which for the case at hand is found from

\[
\det(\rho - \lambda I) = 0 = \det\begin{bmatrix}
\frac{9}{25} - \lambda & \frac{12}{25} e^{i(E_2-E_1)} \\
\frac{12}{25} e^{-i(E_2-E_1)} & \frac{16}{25} - \lambda
\end{bmatrix}
\]

The characteristic equation which results is $\lambda(\lambda - 1) = 0$ and the eigenvalues are 1 and 0, so that $\langle S \rangle$ becomes

\[
\langle S \rangle = -k \text{Tr}\left(\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \ln(1) & 0 \\ 0 & \ln(0) \end{bmatrix}\right) = -k \text{Tr}\left(\begin{bmatrix} 0 & (0)\ln(0) \\ 0 & (0)\ln(0) \end{bmatrix}\right) = 0
\] (3.49)

We assume $0\ln 0$ to vanish and $\langle S \rangle = 0$ as we would expect for a pure state. Had our example been an impure state, the calculation of eigenvalues would have obtained two positive real values that were greater than zero and less than unity. The use of equation (3.47) would have resulted in a positive, non-zero expectation value for the system entropy.

As shown in equation (3.17) the density operator for an impure state can in QSM be considered a linear combination of individual pure-state density operators. The $p_i$ represent the eigenvalues, or $\lambda_i$ of $\rho$. The pure state density operators themselves may consist of one, or a linear combination of more than one energy eigenvectors. Given a $\rho$ in the form of equation (3.17), one can combine all of the weighted pure-state matrices together and then apply equation (3.23), to calculate quantities such as the energy $\langle E \rangle$ of the system or instead sum the $\langle E \rangle$ for each pure state, weighted by its $p_i$ value, i.e.,

\[
\langle E \rangle = \sum_{i=1}^{n} p_i \langle E \rangle_i
\] (3.50)

where $\langle E \rangle_i$ are the expectation values of each pure state.

Although mathematically the density, or state operator for an impure state can be thought of a sum of individual pure state density operators (see equation 3.18), the interpretation offered by IQT rejects this notion. IQT asserts that at all times there is but one and only one state for the system, and that this state is described by the density operator of a homogenous ensemble of
systems, where each member of the ensemble is in an identical impure state. Such a concept is not hard to grasp considering that in QM the state or wave function is the sum of individual eigenvectors, and one does not consider these individual “eigenstates” to represent the state of the system as a whole.

### 3.3 Density Operators, Projection Operators and their Dependence on Space and Time

A closer look is taken at how projection operators are used with density operators to provide the probabilities for measurement results. The definitions of these operators are broadened to include time and spatial variables.

The time independent state vector \( |\Psi(0)\rangle \) solution to the Schrödinger equation can be expressed as an explicit function of time as follows:

\[
|\Psi(t)\rangle = \exp(-iHt/\hbar)|\Psi(0)\rangle
\]  

(3.51)

The time dependent density operator for a pure state then becomes

\[
\rho(t) = |\Psi(t)\rangle \langle \Psi(t)|
\]  

(3.52)

and evolves in time according to

\[
\frac{d\rho}{dt} = \frac{d}{dt} \left( |\Psi\rangle \langle \Psi| + |\Psi\rangle \frac{d}{dt} \langle \Psi| \right)
\]

(3.53)

Substituting equation (3.51) and differentiating yields

\[
\frac{d\rho}{dt} = \frac{-i}{\hbar} \frac{d}{dt} \left( |\Psi\rangle \langle \Psi| \right) = \frac{-i}{\hbar} H |\Psi\rangle \langle \Psi| + \langle \Psi| \exp(-iHt/\hbar)|\Psi(0)\rangle \exp(iHt/\hbar) |\Psi(0)\rangle \frac{i}{\hbar} H 
\]

(3.54)

Resubstituting equation (3.51) produces

\[
\frac{d\rho}{dt} = \frac{-i}{\hbar} \left( H |\Psi\rangle \langle \Psi| - |\Psi\rangle \langle \Psi| H \right)
\]

(3.55)

Using equation (3.52) and the definition of the Poisson brackets one arrives at

\[
\frac{d\rho}{dt} = \frac{-i}{\hbar} (H\rho - \rho H) = \frac{i}{\hbar} [\rho, H]
\]

(3.56)

which is a form of the time dependent Schrödinger equation that is also known as the von Neumann equation of motion.

The time independent state vector \( |\Psi(0)\rangle \) can be expanded in terms of its eigenvectors \( |u_i\rangle \) as
\[ |\Psi(0)\rangle = \sum_i c_i(0) |u_i\rangle, \]  
and by substituting equation (3.51) we obtain
\[ |\Psi(t)\rangle = \sum_i c_i(0) \exp(-iE_i t/\hbar) |u_i\rangle = \sum_i c_i(t) |u_i\rangle \]  
where
\[ c_i(t) = c_i(0) \exp(-iE_i t/\hbar) \]  
The probability of obtaining the energy eigenvalue \( E_i \) after an energy measurement is then given by
\[ c_i^* c_i = |c_i(0)|^2 \]  
which is constant in time. Note also that the eigenvectors of \( |\Psi(t)\rangle \), i.e., the \( |u_i\rangle \), do not vary in time since the Hamiltonian for the system is assumed to be time invariant. Furthermore, the time dependent state vector \( |\Psi(t)\rangle \) can be converted into a function of both \( x \) and \( t \) by taking the scalar product of \( |\Psi\rangle \) with the vector \( \langle x | \) in Euclidian space, i.e.,
\[ \Psi(x,t) = \langle x | \Psi(t) \rangle \]  
Similarly, the basis set for \( |\Psi\rangle \) becomes
\[ u_i(x) = \langle x | u_i \rangle \]  
To find the probability of measuring the energy eigenvalue \( E_i \) for a system that is in a pure state, equation (3.26) is used resulting in
\[ \text{Prob}(E_i) = \text{Tr}[\rho |u_i\rangle \langle u_i|] = \langle u_i | \rho | u_i \rangle \]  
Where \( |u_i\rangle \langle u_i| \) is the corresponding projection operator for the Hamiltonian. Substituting the time dependent density matrix as given by equation (3.52) leads to
\[ \text{Prob}(E_i) = \text{Tr}[|\Psi(t)\rangle \langle \Psi(t)| u_i \rangle \langle u_i|] = \langle \Psi(t) | u_i \rangle \text{Tr}[|\Psi(t)\rangle \langle \Psi(t)|] \langle u_i | \Psi(t) \rangle = \langle \Psi(t) | u_i \rangle \langle u_i | \Psi(t) \rangle \]  
The eigenvectors \( |u_i\rangle \) are orthonormal so that the inner product between any two vectors is such that \( \langle u_i | u_j \rangle = \delta_{ij} \) where \( \delta_{ij} \) is 1 if \( i = j \) and 0 if \( i \neq j \). Using this property together with equation (3.63) leads to
\[ \langle \Psi(t) | u_i \rangle \langle u_i | \Psi(t) \rangle = \sum_j c_j(t) \langle u_j | u_i \rangle^2 = |c_i|^2 \]  
which is a constant in time. Thus, the modulus squared of the inner product of \( \langle \Psi \rangle \) and \( |u_i\rangle \) \( |u_i\rangle \) is identical to the modulus squared of the coefficient for the \( i^{th} \) eigenvector of \( \Psi(t) \). We could also have used equation (3.26) i.e.,
\[
\text{Prob}(E_i) = \langle u_i | \rho | u_i \rangle = \langle u_i | \Psi(t) \rangle \langle \Psi(t) | u_i \rangle = |\langle \Psi(t) | u_i \rangle|^2 \tag{3.66}
\]
to achieve the same result.

Now to convert the inner product \( \langle \Psi(t) | u_i \rangle \) from Dirac notation to its equivalent integral definition, we insert the identity,

\[
I = \int_{-\infty}^{\infty} |x\rangle \langle x| dx
\tag{3.67}
\]
Using equation (3.67) together with the complex conjugate of equation (3.64) along with equation (3.62) produces

\[
\langle \Psi(t) | u_i \rangle = \langle \Psi(t) | \int_{-\infty}^{\infty} |x\rangle \langle x| dx \rangle u_i \rangle = \int_{-\infty}^{\infty} \langle \Psi(t) | x \rangle \langle x | u_i \rangle dx = \int_{-\infty}^{\infty} \Psi^*(x,t) u_i(x) dx \tag{3.68}
\]
Substitution into equation (3.66) yields

\[
\text{Prob}(E_i) = \left| \int_{-\infty}^{\infty} \Psi^*(x,t) u_i(x) dx \right|^2 \tag{3.69}
\]

To find the likelihood of getting a certain value of position when a position measurement is made for a pure state, equations (3.26) and (3.67) are used to get

\[
\text{Prob}(x) = \text{Tr}\left( \rho \langle x | \langle x| \right) = \text{Tr}\left( \langle \Psi(t) | x \rangle \langle x | \Psi(t) \rangle \right) = |\langle \Psi(t) | x \rangle|^2 = |\Psi(x,t)|^2 \tag{3.70}
\]
As expected, calculating \( \langle x | \rho(t) | x \rangle \) gives the same answer.

To obtain the probability of a measurement outcome for a system in a mixed state, the appropriate projection operators are used in (3.26) exactly as before. Only the definition of the density operator has changed. For the case where the density operator and the Hamiltonian operator share the same eigenvectors, both operators can simultaneously be made to be diagonal. The eigenvectors are just the \( |u_i\rangle \), i.e., the basis vectors of the Hamiltonian operator. The density operator can then be expressed as

\[
\rho(t) = \sum_j p_j(t) |\Psi_j(t)\rangle \langle \Psi_j(t)| = \sum_j p_j(t) |u_j\rangle \langle u_j|
\tag{3.71}
\]
Noting that the trace of the sum is the sum of the traces, using the result of equation (3.71), the probability of measuring a given energy eigenvalue \( E_i \) is

\[
\text{Prob}(E_i(t)) = \text{Tr}\left( \rho |u_i\rangle \langle u_i| \right) = \text{Tr}\left( \sum_j p_j(t) |u_j\rangle \langle u_j| |u_i\rangle \langle u_i| \right) = \sum_j p_j(t) \langle u_j | u_i \rangle \text{Tr}(|u_j\rangle \langle u_i|) \tag{3.72}
\]
Since the \( |u_i\rangle \) are orthonormal \( \langle u_i | u_i \rangle = \text{unity} \) as is \( \text{Tr}(|u_i\rangle \langle u_i|) \) and thus
\[
\text{Prob}(E_i(t)) = p_i(t) |\langle u_i | u_i \rangle|^2 = p_i(t) \tag{3.73}
\]

In a similar fashion the probability that a given position value is measured is
\[
\text{Prob}(x(t)) = \text{Tr}(\rho(t) |x\rangle \langle x|) = \text{Tr} \left( \sum_j p_j(t) |u_j \rangle \langle u_j| x \rangle \langle x| \right) = \sum_j p_j(t) |\langle u_j | x \rangle|^2 = \sum_j p_j(t) |u_j(x)|^2 \tag{3.74}
\]

For a mixed state where \(\rho\) and \(H\) do not commute and thus do not share the same eigenvectors
\[
\text{Prob}(E_i(t)) = \text{Tr}(\rho |u_i \rangle \langle u_i|) = \text{Tr} \left( \sum_j p_j(t) |\Psi_j(t) \rangle \langle \Psi_j(t)| u_i \rangle \langle u_i| \right) = \sum_j p_j(t) |\langle \Psi_j(t) | u_i \rangle|^2 \tag{3.75}
\]

Inserting equation (3.64) results in the equivalent integral form i.e.,
\[
\text{Prob}(E_i(t)) = \left| \int_{-\infty}^{\infty} \Psi^*(x,t) u_i(x) dx \right|^2 \tag{3.76}
\]
The vectors \(|\Psi_j(t) \rangle\) expanded in their Hamiltonian eigenbasis as shown in equation (3.58) are
\[
|\Psi_j(t) \rangle = \sum_k c_{jk}(t) |u_k \rangle \tag{3.77}
\]

where
\[
c_{jk}(t) = \langle u_k | \Psi_j(t) \rangle \tag{3.78}
\]

Using the complex conjugate of equation (3.77) the probability of a measurement yielding \(E_i\) given by equation (3.75) is then
\[
\text{Prob}(E_i(t)) = \sum_j p_j(t) |\langle \Psi_j(t) | u_i \rangle|^2 = \sum_j p_j(t) \left| \sum_k c_{jk}^*(t) |u_k \rangle \langle u_i| \right|^2 = \sum_j p_j(t) \sum_k |c_{jk}(t)|^2 \delta_{ki} \tag{3.79}
\]

The second sum over index \(k\) vanishes since only one term survives due to the orthogonality of the \(|u\rangle\) basis. For position, the probability that a given position value is measured when \(\rho\) and \(H\) do not commute is
\[
\text{Prob}(x(t)) = \text{Tr}(\rho(t) |x\rangle \langle x|) = \text{Tr} \left( \sum_j p_j(t) |\Psi_j(t) \rangle \langle \Psi_j(t)| x \rangle \langle x| \right) \tag{3.76}
\]
\[
\psi_j(t) = \sum_j p_j(t) |\psi_j(t)\rangle \langle x | = \sum_j p_j(t) |\psi_j(t)\rangle \langle x |^2 \\
= \sum_j p_j(t) |\psi_j^*(x,t)|^2
\]

The expansion for \( |\psi_j(x,t)\rangle \) is

\[
|\psi_j(x,t)\rangle = \langle x | \psi_j(t) \rangle = \sum_k c_{jk}(t) \langle x | u_j \rangle = \sum_j c_{jk}(t) u_k(x)
\]

Where

\[ c_{jk}(t) = \langle u_k(x) | \psi_j(x,t) \rangle \]

After substituting equation (3.81) into equation (3.80) the result is

\[
\text{Prob}(x(t)) = \sum_j p_j(t) \left| \sum_k c_{jk}^*(t) u_k^*(x) \right|^2 = \sum_j p_j(t) \left| \sum_k c_{jk}(t) u_k(x) \right|^2
\]

In all of the above cases except for the case of a pure state, the time dependence of the system probabilities and eigenvalues of the density (state) operator vary separately from that of the cyclic time evolution of the phase components of the density operator elements. The time dependent Schrödinger equation is able to show how the phase components change in time but not the probabilities or eigenvalues of the state operator. A more general equation of motion such as that of IQT is needed to predict how the eigenvectors of \( \rho \) and hence how the entropy of a system evolves in time.

### 3.4 Derivation of the Beretta Equation (IQT Equation of Motion)

Using the Principle of Steepest Entropy Ascent coupled with geometric arguments based on manifolds, Beretta has developed an equation of motion (Beretta 1981) that is able to describe the evolution of a quantum system along a trajectory from a non-equilibrium state that has entropy to a final state of maximum entropy at stable equilibrium. The equation obeys all of the expected requirements of both QM and Thermodynamics, including the Second Law of Thermodynamics. The derivation of the Beretta equation is also found in Beretta (1986), Gheorghiu-Svirchevski (2001) who used a variational formulation, Beretta (2001), Beretta (2006a,b) and Beretta (2009a). Although all of the derivations by Beretta are equivalent, they vary in form and notation.
The following derivation is a summary that uses the notation of Beretta (2009a). The entropy of the system is a function of $\rho$, the density operator. To ensure that the entropy always stays at values equal to or greater than zero, $\rho$ for convenience is defined as

$$\rho = \gamma^+ \gamma$$

(3.84)

where $\gamma$ can be interpreted as a Hermitian square root of the density operator. Entropy is therefore also a function of $\gamma$,

$$\langle S \rangle = \langle S(\rho) \rangle = \langle S(\gamma) \rangle$$

(3.85)

Let the vector $b$ represent the gradient with respect to $\gamma$ defined as

$$b = \frac{\partial}{\partial \gamma} \langle S \rangle$$

(3.86)

where vector $b$ is entropy change for the system and is to be maximized.

The scalar product, or inner product for the vector spaces under consideration is defined for operators $A$ and $B$ as

$$(A \mid B) = A \cdot B = \frac{1}{2} \text{Tr} \left( A^+ B + B^+ A \right)$$

(3.87)

Now, let $g_0, g_1, \ldots, g_n$ represent a subset of vectors in a larger real vector space of linear operators $\mathcal{L}(H)$, which are not necessarily self adjoint but possess a real scalar product. The set $g_0, g_1, \ldots, g_n$ are gradients that will be used to apply the constraints to the system as will be seen later. Let $L(g_0, g_1, \ldots, g_n)$ be a linear manifold (or subspace) of $\mathcal{L}$ that is spanned by $g_0, g_1, \ldots, g_n$. Any vector in the larger vector space can be decomposed as is seen in figure 3.1 into a component that is contained in, that is, parallel to $L(g_0, g_1, \ldots, g_n)$ and a component that is orthogonal or perpendicular to $L(g_0, g_1, \ldots, g_n)$. Thus, the vector $b$ above is

$$b = b_L + b_\perp$$

(3.88)

where $b_L = b_{L(g_0, g_1, \ldots, g_n)}$ stands for the unique projection of $b$ onto the linear manifold $L(g_0, g_1, \ldots, g_n)$.

Because $b_L$ is contained in $L(g_0, g_1, \ldots, g_n)$, the dot product of $b_L$ with any other vector $g$ that is also in $L(g_0, g_1, \ldots, g_n)$ is the same as the dot product of $g$ with the entire vector $b$ since the orthogonal component $b_\perp$ does not contribute. Thus

$$g \cdot b_{L(g_0, g_1, \ldots, g_n)} = g \cdot b$$

(3.89)

for every $g$ in $L(g_0, g_1, \ldots, g_n)$. 
Figure 3.1. The vector components of \( b \), the gradient vector of entropy change. Part of \( b \) is contained in the manifold \( L \) which contains the constraints while another component of \( b \) is perpendicular to \( L \). The gradients \( g_0 \) and \( g_1 \) are the constraint vectors that define the manifold \( L \).

Given another, different set of linearly independent vectors \( h_1, \ldots, h_r \) that span the manifold \( L \), where \( r \leq n \), \( b_L \) can be expanded in terms of these new vectors as

\[
b_L = \sum_{i=1}^{r} \beta_i h_i
\]  

(3.90)

As above, the \( b_\perp \) component does not contribute to scalar products of the \( h_i \) vectors either so,

\[
b_L \cdot h_j = b \cdot h_j
\]  

(3.91)

and

\[
\sum_{i=1}^{r} \beta_i h_i \cdot h_j = b \cdot h_j
\]  

(3.92)

for \( j = 1,2,\ldots, r \). The \( h_i \cdot h_j \) products form a matrix

\[
M(h_1,\ldots,h_r) = \begin{bmatrix}
h_1 \cdot h_1 & \cdots & h_r \cdot h_1 \\
\vdots & \ddots & \vdots \\
h_1 \cdot h_r & \cdots & h_r \cdot h_r
\end{bmatrix}
\]  

(3.93)

so that

\[
\sum_{i=1}^{r} \beta_i M(h_1,\ldots,h_r) = b \cdot h_j
\]  

(3.94)

The \( \beta_i \) can be determined since the \( h_i \) are linearly independent and the inverse of \( M(h_1,\ldots,h_r) \) exists (see also Beretta (1986) for details).

\[
\beta_i = \sum_{j=1}^{r} b \cdot h_j [M(h_1,\ldots,h_r)^{-1}]_{ji}
\]  

(3.95)

Using this result in the expansion for \( b_L \) the following result is obtained:

\[
b_L = \sum_{i=1}^{r} \sum_{j=1}^{r} (b \cdot h_j) [M(h_1,\ldots,h_r)^{-1}]_{ji} h_i
\]  

(3.96)

As indicated above, the vectors \( g_0, g_1, \ldots, g_n \) are gradients that represent the constraints of the system. A common set of constraints include: \( g_0 \), the gradient vector associated with the
normalization constraint, \( \text{Tr}(\rho) = 1 \), and \( g_1 \), the gradient vector associated with maintaining the energy of an isolated system constant,

\[
\langle H \rangle = \text{Tr} \, \rho H = \gamma H \cdot \gamma
\]  

where the identity in equation (3.87) has been used. Correspondingly, \( h_1, \ldots, h_r \) are related to the generators of the motion \( H \) and \( I \) for an isolated system, namely, \( h_1 = 2\gamma H \); and, \( h_r = 2\gamma I = 2\gamma \).

The \( h_i \) are chosen so that in this case \( h_r = h_2 \) is the gradient of the normalization constraint, i.e.,

\[
\text{Tr}(\rho) = \gamma \cdot h_2 / 2
\]  

The system energy is also expressed in terms of the \( h_i \) by

\[
\langle H \rangle = \text{Tr} \, \rho H = h_1 \cdot h_2 / 4 = \gamma H \cdot \gamma
\]  

For an open system, additional \( h_i \) related to additional generators of the motion are

\[
h_{2, \ldots, r-1} = \gamma N_1 \cdot \gamma, \ldots, \gamma N_k \cdot \gamma,
\]

where the \( N_j \) are the particle number operators for constituents \( 1, \ldots k \). In this case, the expectation values of the a particle number operators in terms of the \( h_i \) are given by

\[
\langle N_j \rangle = \text{Tr} \, \rho N_j = h_j \cdot h_r / 4 = \gamma N_j \cdot \gamma
\]  

where \( j = 2, \ldots, r-1 \).

To obtain the Beretta equation of motion, which governs the time evolution of the density operator \( \rho \), it is convenient to recast the above geometric interpretation along with the constraints in terms of inner products. The time evolution of \( \rho \), i.e., \( \dot{\rho} \) is replaced by the time evolution of \( \gamma \), i.e., \( : \dot{\gamma} : \).

Next, the trace of the state operator \( \rho \) is recast using equation (3.80)

\[
\text{Tr}(\rho) = \text{Tr}(\gamma^+ \gamma) = \frac{1}{2} \text{Tr}(\gamma^+ \gamma + \gamma^+ \gamma) = \gamma \cdot \gamma
\]  

Note that one can take the gradient if needed, that is,

\[
\frac{\partial}{\partial \gamma} \text{Tr}(\rho) = 2\gamma
\]  

The conservation of the normalization requires that

\[
\frac{d}{dt} \text{Tr}(\rho) = 0
\]  

Using equation (3.98), the time dependence of the normalization can be written as

\[
0 = \frac{d}{dt} \text{Tr} \, \rho = \frac{d}{dt} (\gamma \cdot \gamma) = \dot{\gamma} \cdot \gamma + \gamma \cdot \dot{\gamma} = 2\gamma \cdot \dot{\gamma} = \frac{\partial}{\partial \gamma} \text{Tr} \, \rho \cdot \dot{\gamma} = g_0 \cdot \dot{\gamma}
\]
where
\[ g_0 = \frac{\partial}{\partial \gamma} \langle \text{Tr} \rho \rangle = 2\gamma \] (3.105)

For the constraint \( \text{Tr}(\rho) = 1 \) to be enforced, it is necessary that \( g_0 \cdot \dot{\gamma} = 0 \), which implies that \( \dot{\gamma} \perp g_0 \) or equivalently \( \gamma \perp \gamma \). Since the entropy is a function of \( \gamma \), the trajectory of \( \langle S \rangle \) the expectation value of the entropy, must be contained in the component of \( b \) that is perpendicular to the vector \( g_0 \) in the manifold \( L \).

Now, using equations (3.84), (3.87), the cyclic property of the trace and the Hermiticity of \( \rho \) and \( H \), the value of \( \langle H \rangle \) the energy can be written as
\[
\langle H \rangle = \text{Tr} \rho H = \frac{1}{2} \text{Tr} (\rho H + \rho H^*) = \frac{1}{2} \text{Tr} \left( \gamma^+ \gamma H + \gamma^+ \gamma^+ H^+ \right) = \frac{1}{2} \text{Tr} \left( \gamma^+ \gamma H + \gamma^+ \gamma^+ H^+ \right)
\]
(3.106)

and its gradient as
\[
\frac{\partial}{\partial \gamma} \langle H \rangle = 2\gamma H
\] (3.107)
so that the time derivative of \( \langle H \rangle \) is
\[
\frac{d}{dt} \langle H \rangle = \frac{d}{dt} (\gamma H \cdot \gamma) = \frac{d}{dt} (\gamma H \cdot \gamma) \frac{d\gamma}{dt} = 2\gamma H \cdot \dot{\gamma} = \frac{\partial}{\partial \gamma} \langle H \rangle \cdot \dot{\gamma} = g_1 \cdot \dot{\gamma}
\] (3.108)

Constant \( \langle H \rangle \) with time requires that
\[
\frac{d}{dt} \langle H \rangle = g_1 \cdot \dot{\gamma} = 0
\] (3.109)
which implies that \( \gamma \perp g_1 \) and the change in entropy of the system must be perpendicular to \( g_1 \) as well \( g_0 \). Thus, the evolution of the entropy is perpendicular to the entire manifold \( L \). If in the case of an isolated system something more than \( b_\perp \) were used, the constraints would be violated.

The time evolution of the system entropy can now be constructed. Using procedures identical to developing the energy constraint one begins with
\[
\langle S \rangle = \text{Tr}(\rho S) = \gamma S \cdot \gamma
\] (3.110)
The time derivative of \( \langle S \rangle \) then is
\[
\frac{d}{dt} \langle S \rangle = 2\gamma \langle S \rangle \cdot \dot{\gamma}
\] (3.111)
Recalling equations (3.86) and (3.106), the vector \( b \) can be written as
\[ b = \frac{\partial}{\partial \gamma} \langle S \rangle = 2\gamma \langle S \rangle \]  

(3.112)

Combining these last two expressions, results in

\[ \frac{d}{dt} \langle S \rangle = b \cdot \dot{\gamma} \]  

(3.113)

The maximum local entropy change with time as per Beretta’s hypothesis of Steepest Entropy Ascent occurs when the dot product \( b \cdot \dot{\gamma} \) is maximal, and this occurs when

\[ \frac{d}{dt} \langle S \rangle = \dot{\gamma} \cdot \dot{\gamma} \]  

(3.114)

that is, when

\[ b = \dot{\gamma} \]  

(3.115)

However, the constraints must be applied which, from the previous analysis, means that the constraints are satisfied only as long as just the perpendicular component of \( b \) is used. The result is the Beretta equation i.e.,

\[ \dot{\gamma} = b_\perp \]  

(3.116)

Since \( b \) and \( b_L \) are known, the quantity \( b_\perp \) is

\[ b_\perp = b - b_L \]  

(3.117)

The Beretta equation, with the dissipation term \( \dot{\gamma}_D \) only (i.e. \( \dot{\gamma}_H \)) without the von Neumann term becomes,

\[ \dot{\gamma} = \dot{\gamma}_D = b - b_L \]  

(3.118)

The desired evolution in time of the entropy in terms of the evolution in time of the density operator has been obtained. Relations for both \( b \) and \( b_L \) developed earlier can be expressed as ratios of Gramm determinants where

\[ b_L = -\frac{\det M(0,b,h_1,\ldots,h_r)}{\det M(h_1,\ldots,h_r)} \]  

(3.119)

The denominator is strictly positive because the \( h_i \) vectors are linearly independent. Equation (3.116) is equivalent to equation (3.96) developed earlier. Using the former, equation (3.115) can now be written as

\[ \dot{\gamma} = -\frac{\det M(b,h_1,\ldots,h_r)}{\det M(h_1,\ldots,h_r)} \]  

(3.120)

Defining the deviation vectors,

\[ \Delta h_j = \left( h_j - h_r \langle H_j \rangle \right)/2 \]  

(3.121)
where the \( H_j \) for \( j = 1, \ldots, r - 1 \) are \( H_1 = H, H_2 = N_1, \ldots, H_{r-1} = N_k \) and \( B \) is equal to the entropy operator \( S \), one can rewrite equation (3.120) as

\[
\dot{\gamma} = -\frac{\det M(\Delta b, \Delta h_1, \ldots, \Delta h_r)}{\det M(\Delta h_1, \ldots, \Delta h_r)}
\]  
(3.123)

Equation (3.123) is equivalent to the more well known IQT dissipation operator \( D \) shown in equations (2.2) and (2.7). As shown in Beretta, (2009), equation (3.123) can also be expressed in the form of a non-equilibrium Massieu function which has the units of entropy and is defined as

\[
M = S - \frac{H}{\theta_H}
\]  
(3.124)

where \( S \) and \( H \) are entropy and Hamiltonian operators respectively with \( \theta_H \) representing a non-equilibrium temperature. The derivation of equation (3.124) will be explained in greater detail in Section 4.3.1 of Chapter 4 with the development of an IQT dissipation operator for an open system. Equation (3.124) can be shown in the form of deviances as

\[
\Delta M = \Delta S - \frac{\Delta H}{\theta_H}
\]  
(3.125)

where

\[
\Delta M = M - \langle M \rangle I
\]  
(3.126)

Similarly,

\[
\Delta S = S - \langle S \rangle I
\]  
(3.127)
\[
\Delta H = H - \langle H \rangle I
\]  
(3.128)

The variance for the operator \( M \) is defined to be

\[
\langle \Delta M \Delta M \rangle = \text{Tr} \, \rho(\Delta M)^2
\]  
(3.129)

Substitution of equation (3.126) yields

\[
\langle \Delta M \Delta M \rangle = \text{Tr} \, \rho(\Delta M)^2 = \text{Tr} \, \rho M^2 - (\text{Tr} \, \rho M)^2 = \langle M^2 \rangle - \langle M \rangle^2
\]  
(3.130)

The quantity \( \theta_H \) may vary with time and is defined as

\[
\theta_H(\rho) = \frac{\langle \Delta H \Delta H \rangle}{\langle \Delta H \Delta S \rangle}
\]  
(3.131)

where \( \langle \Delta H \Delta H \rangle \) and \( \langle \Delta H \Delta S \rangle \) are variances defined as in equation (3.130).

Using the \( \Delta M \) operator the IQT equation of motion can be expressed as
\[ \dot{\rho} = \dot{\rho}_D = \left( \frac{1}{2\tau_D \sqrt{\langle \Delta M \Delta M \rangle}} \right) \{\Delta M, \rho\} \]  

(3.132)

with

\[ \frac{1}{\tau(\rho)} = \left( \frac{1}{2\tau_D \sqrt{\langle \Delta M \Delta M \rangle}} \right) \]

(3.133)

Derived in Beretta (2009a), equation (3.133) is based on the lower limit for the time functional \( \tau(\rho) \) set by the Heisenberg time-energy relation. The magnitude of the \( \tau(\rho) \) limit varies with the state of the system \( \rho \) along the system trajectory toward stable equilibrium. In practice \( \tau \) may be a constant and far larger than the theoretical limit. The smaller the \( \tau \), the faster the system evolves over time.

The term in braces on the right hand side equation (3.132) is an anti-commutator which is defined as

\[ \{\Delta M, \rho\} = \frac{1}{2} (\Delta M \rho + \rho \Delta M) \]

(3.134)

and represents the part of the dissipation operator derived using a constrained steepest entropy path on a manifold as discussed above.

3.5 Phenomenological Modeling Equations for the Density Operator of a Coupled System or a System Interacting with the Environment

Recently, the Beretta equation, which describes the dynamics of isolated systems, has been extended to situations where the system interacts with the environment (Beretta, 2008; Beretta, 2009a). Sections 3.5 - 3.7 present brief summaries of these developments. The form of the resulting external contributions to the time rate of change of the state operator is similar to that of the dissipation term for an isolated system. The major distinction is that the non-equilibrium temperature term \( \theta \) in the Massieu-like relation is defined differently. The IQT equation of motion minus the von Neumann and dissipation terms is then written as

\[ \dot{\rho} = \dot{\rho}_Q = \left( \frac{1}{2\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \right) \{\Delta G, \rho\} \]

(3.135)

where

\[ G = S - \frac{H}{\theta(\rho)} \]

(3.136)
\[ \Delta G = \Delta S - \frac{\Delta H}{\theta(\rho)} \]  
(3.137)

\[ \Delta G = G - \langle G \rangle I \]  
(3.138)

and

\[ \langle \Delta G \Delta G \rangle = \langle G^2 \rangle - \langle G \rangle^2 \]  
(3.139)

The operator \( G \) like \( M \) has the units of entropy and is another non-equilibrium Massieu operator. The symbol \( \theta \) is an additional non-equilibrium temperature which may vary with time. Equation (3.136) may govern the change of energy, entropy or mass depending on the chosen external effect, an effect which may be phenomenological as opposed to fundamental in its description.

Now, to formulate rate of change of the energy of a system due to some interaction with the environment (or some other system), we first formulate the time rate of change of the energy as

\[ \frac{d\langle H \rangle}{dt} = \frac{d}{dt} \text{Tr}(\rho H) = \text{Tr} \frac{d}{dt} (\rho H) = \text{Tr}(\dot{\rho} H + \rho \dot{H}) = \text{Tr}(\dot{\rho} H) \]  
(3.140)

The term \( \rho \dot{H} \) is zero since it is assumed that the Hamiltonian energy structure of the system is not altered by the interaction i.e., \( H \) is not a function of time. In a similar vein, the time rate of change of the expectation value of the deviation operator \( \Delta H \)

\[ \frac{d\langle \Delta H \rangle}{dt} = \text{Tr} \dot{\rho} \Delta H = \text{Tr} \dot{\rho} (H - \langle H \rangle I) = \text{Tr} \dot{\rho} H - \langle H \rangle \text{Tr} \dot{\rho} = \text{Tr} \dot{\rho} H \]  
(3.141)

Thus one concludes that

\[ \frac{d\langle \Delta H \rangle}{dt} = \frac{d\langle H \rangle}{dt} \]  
(3.142)

Substituting equation (3.136) for \( \dot{\rho} \),

\[ \frac{d\langle H \rangle}{dt} = \text{Tr} \dot{\rho} \Delta H = \frac{1}{2\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \text{Tr} \{\Delta G, \rho\} \Delta H \]  
(3.143)

The order of the operators within the trace can be cycled so that

\[ \frac{d\langle H \rangle}{dt} = \frac{1}{2\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \text{Tr} \rho \{\Delta H, \Delta G\} = \frac{1}{\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \langle \Delta H \Delta G \rangle \]  
(3.144)

Using the expression for \( \Delta G \), equation (3.138) we find

\[ \langle \Delta H \Delta G \rangle = \langle \Delta H \Delta S \rangle - \frac{1}{\theta} \langle \Delta H \Delta H \rangle \]  
(3.145)
Using equation (3.127) for $\theta_H$, equation (3.145) can be rewritten as

$$\langle \Delta H \Delta G \rangle = \langle \Delta H \Delta H \rangle \left( \frac{1}{\theta_H} - \frac{1}{\theta} \right)$$

(3.147)

So that the time rate of change of the energy $\langle H \rangle$ becomes

$$\frac{d}{dt} \langle H \rangle = - \frac{\langle \Delta H \Delta H \rangle}{\tau_G \sqrt{{\Delta G \Delta G}}} \left( \frac{1}{\theta_H} - \frac{1}{\theta} \right)$$

(3.148)

The time rate of change of the entropy is derived using a similar procedure, beginning with

$$\frac{d}{dt} \langle S \rangle = \frac{d}{dt} \text{Tr}(\rho S) = \text{Tr} \frac{d}{dt} \left( \rho \frac{d}{dt} \right) \left( \rho S + \rho \dot{S} \right) = \text{Tr}(\dot{\rho} S)$$

(3.149)

Where the $\text{Tr}(\rho \dot{S})$ term disappears since

$$\text{Tr}(\rho \dot{S}) = \text{Tr} \left( \rho \left( - \frac{k_b}{\rho} \right) \right) = - k_b \frac{d}{dt} \text{Tr}(\rho) = 0$$

(3.150)

As before for $H$ and $\Delta H$, $\Delta S$ can be exchanged for $S$ and thus

$$\frac{d}{dt} \langle \Delta S \rangle = \frac{d}{dt} \langle S \rangle = \text{Tr}(\dot{\rho} \Delta S) = \text{Tr}(\dot{\rho} S)$$

(3.151)

Defining yet a new non-equilibrium temperature

$$\theta_S(\rho) = \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle}$$

(3.152)

and using

$$\langle \Delta S \Delta G \rangle = \langle \Delta S \Delta S \rangle \frac{1}{\theta} \langle \Delta S \Delta H \rangle$$

(3.153)

the time rate of change of the entropy $\langle S \rangle$ can be written as

$$\frac{d}{dt} \langle S \rangle = - \frac{\langle \Delta S \Delta S \rangle}{\tau_G \sqrt{{\Delta G \Delta G}}} \left( 1 - \frac{\theta_S}{\theta} \right)$$

(3.154)

where use of equation (3.135) for $\rho$ has been made. It should be noted that $\theta_S$ and $\theta_H$ both approach the equilibrium temperature as stable equilibrium is reached.

Alternatively, valid interactions with the environment or some other system may also be formulated in terms of operators that have units of energy such as

$$F = H - \theta S$$

(3.155)

The equation of motion for the interaction then becomes (minus the von Neumann and dissipation terms)
\[
\dot{\rho} = \dot{\rho}_Q = \left( \frac{1}{2\tau_G \sqrt{\langle \Delta F \Delta F \rangle}} \right) \{\Delta F, \rho\}
\]

while
\[
\frac{d \langle H \rangle}{dt} = -\frac{\langle \Delta H \Delta H \rangle}{\tau_F \sqrt{\langle \Delta F \Delta F \rangle}} \left( 1 - \frac{\theta}{\theta_H} \right)
\]

and
\[
\frac{d \langle S \rangle}{dt} = \frac{\langle \theta_s - \theta \Delta S \Delta S \rangle}{\tau_F \sqrt{\Delta F \Delta F}}
\]

The operator \( F \) can be interpreted as a non-equilibrium Helmholtz free energy operator. The entropy and energy forms of interaction are related via
\[
\frac{\langle \Delta F \Delta F \rangle}{\langle \Delta G \Delta G \rangle} = \frac{\langle \Delta H \Delta H \rangle}{\langle \Delta S \Delta S \rangle} = \theta_H \theta_S
\]

System trajectories are the same regardless of whether the entropy or energy form is used.

### 3.6 Isentropic Extraction of Adiabatic Availability for an Isolated System

The adiabatic availability for a system in a non-equilibrium state is the largest amount of energy that can be extracted as work without leaving any other effects external to the system. It is assumed that the Hamiltonian for the system remains unchanged, which precludes adiabatic work processes due to changes in volume. The work extraction may occur by means of a cyclic device (heat engine) and so in principle is by means of a reversible process. The following development is also from Beretta (2009a). The adiabatic availability, \( \langle \Psi \rangle \) (not the same as the state vector of QM) is defined as
\[
\langle \Psi \rangle = \langle H \rangle - \langle H \rangle_s
\]

where the expectation value of the energy for the non-equilibrium state is \( \langle H \rangle = \text{Tr}(H \rho) \) and the expectation energy for the stable equilibrium state is \( \langle H \rangle_s = \text{Tr}(H \rho_s(H)) \), with the state matrix for the stable equilibrium state being the canonical distribution given by
\[
\rho_s(H) = \frac{\exp(-\beta_S H)}{\text{Tr} \exp(-\beta_S H)}
\]

where
\[
\beta_S = \frac{1}{k_b T}
\]
and $T$ is the stable equilibrium temperature.

A Helmholtz operator $F$ can be defined to model the smooth adiabatic extraction of energy from a system for use as work with the system entropy held constant, i.e.,

$$F = F_\Psi = H - \theta S$$  \hspace{1cm} (3.162)

with

$$\tau_F = \tau_{F_\Psi}$$  \hspace{1cm} (3.163)

The constant entropy non-equilibrium temperature is given by equation (3.152). Though the process for the extracting the energy is reversible since $S$ is held constant and the process is adiabatic, it is not a unitary process because the eigenvalues of $\rho$ must change during the energy extraction. Since energy is only going out of the system the values of the off diagonal elements must only decrease, i.e., the coherence between the energy levels of the system does not increase.

There may be an infinite number of trajectories that represent smooth extractions of adiabatic availability, a process which is controlled as much by the external interaction as internal system dynamics. One straightforward model is to constrain the system to a steepest energy descent trajectory. The component of the energy gradient orthogonal to $\gamma$ and $S'$, denoted by Beretta (2009a) as $H'_{\perp L(\gamma,S')}$ is

$$H'_{\perp L(\gamma,S')} = \left[ \frac{\langle \Delta H \rangle' \cdot \langle \Delta S \rangle' \cdot \langle \Delta S \rangle'}{\langle \Delta S \rangle' \cdot \langle \Delta S \rangle'} \right] = \langle \Delta H \rangle' - \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle} \langle \Delta S \rangle'$$  \hspace{1cm} (3.164)

where $\langle \Delta H \rangle' = 2\gamma \Delta H$ and $\langle \Delta S \rangle' = 2\gamma \Delta S$ and $H' = 2\gamma H$. Since $H' = 2\gamma H$, the energy operator representing steepest energy descent is

$$H_\perp = H_{\perp L(\gamma,S')} = \langle \Delta H \rangle - \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle} \langle \Delta S \rangle$$  \hspace{1cm} (3.165)

Thus,

$$F = F_{\Psi \perp} = H_\perp - \theta S$$  \hspace{1cm} (3.166)

### 3.7 Non-Equilibrium Heat Interaction with a Reservoir at Temperature $T_R$

A particularly important extension of IQT theory to open systems has been developed by Beretta (2009a), which allows the interaction between a system in a non-equilibrium state and a reservoir at $T_R$ to be modeled. An entropy balance on the reservoir is used to constrain the dynamics, i.e.,
To create the heat interaction operator, the dissipation operator is modified. The Helmholtz form of the dissipation operator can be written as

\[
\hat{\rho}_D = \left( \frac{k_b}{2\tau_F \sqrt{\langle \Delta F \Delta F \rangle}} \right) \{\Delta F, \rho_D\} \tag{3.168}
\]

while the Helmholtz free energy operator is

\[
F = F_D = H - \theta_H S \tag{3.169}
\]

To convert the dissipation operator into a heat interaction operator, Beretta (2009a) transforms the non-equilibrium temperature \( \theta_H \) in equation (3.169) into a new non-equilibrium temperature \( \theta_Q \) that satisfies the constraint of the entropy balance in equation (3.167) as the time evolution of the state of the system proceeds. The resulting heat interaction operator is written as

\[
\hat{\rho}_Q = \left( \frac{k_b}{2\tau_{F_Q} \sqrt{\langle \Delta F \Delta F \rangle}} \right) \{\Delta F, \rho_Q\} \tag{3.170}
\]

The Helmholtz expression for the heat interaction becomes

\[
F = F_{T_Q} = H - \theta_Q S \tag{3.171}
\]

The time constant applicable to the heat interaction is given as

\[
\tau_F = \tau_{F_Q} \tag{3.172}
\]

and the deviation of \( F \) is

\[
\Delta F = \Delta H - \theta_Q \Delta S \tag{3.173}
\]

The non-equilibrium temperature \( \theta_Q \) is determined by substituting the results of equations (3.157) and (3.158) into the entropy balance equation (3.167), which results in

\[
T_Q = \frac{d\langle H \rangle / dt}{d\langle S \rangle / dt} = \frac{\langle \Delta H \Delta H \rangle \left( \frac{1}{\theta_H} - \frac{1}{\theta} \right)}{\langle \Delta S \Delta S \rangle \left( 1 - \frac{\theta_S}{\theta} \right)} = \text{const.} \tag{3.174}
\]

Equation (3.141) is then substituted so that

\[
T_Q = \theta_H \theta_S \left( \frac{\theta - \theta_H}{\theta_H \theta} \right) = \theta \frac{\theta - \theta_H}{\theta - \theta_S} \tag{3.175}
\]

Solving for \( \theta \) gives
\[
\theta = \theta_Q = \theta_S \frac{T_Q - \theta_H}{T_Q - \theta_S} \tag{3.176}
\]

In Beretta (2009), it is assumed that \(T_Q = T_R\) the reservoir temperature, which has been found to produce difficulties. As illustrated in Figure 3.2a by keeping \(T_Q = T_R\), the trajectory of the state of the system is forced to move at a slope corresponding to \(T_R\), which will prevent the state of the system from coming to mutual stable equilibrium with the reservoir. As Figure 3.2b shows, a linear path that intersects the initial and final states of the system trajectory has a slope \(T_Q\) that is not equal to \(T_R\).

In terms of entropy balance equations, the path with the desired slope can be defined in terms of the entropy of the system instead of the entropy of the reservoir.

\[
T_Q = \frac{d\langle H \rangle_{sys}}{d\langle S \rangle_{sys}} = \frac{d\langle H \rangle_{sys}}{d\langle S \rangle_{sys}} \tag{3.177}
\]

The complete entropy balance for the system is then written as

\[
\frac{d\langle S \rangle_{sys}}{dt} = \frac{\dot{Q}}{T_R} + \dot{S}_{irr.sys} = \frac{\dot{Q}}{T_Q} \tag{3.178}
\]

where

\[
\dot{Q} = \frac{d\langle H \rangle_{sys}}{dt} = - \frac{d\langle H \rangle_{res}}{dt} \tag{3.179}
\]

and

\[
\frac{d\langle S \rangle_{res}}{dt} = - \frac{\dot{Q}}{T_R} \tag{3.180}
\]
Equations (3.177) through (3.180) show that the slope $T_Q$ of a path, be it linear or curved that connects the initial and final states for a system undergoing a heat interaction can be defined in terms of an entropy balance for the system while simultaneously satisfying the entropy balance for the reservoir. The derivations of equations (3.174) through (3.176) remain but $T_Q \neq T_R$. In addition, equation (3.178) predicts that entropy must be generated due to irreversibilities as the system moves to mutual stable equilibrium with the reservoir.

3.8 Structure of Carbon Nanotubes

Since carbon nanotubes (e.g., Harris, 2009; Jorio, Dresselhaus and Dresselhaus, 2008; Saito and Zettl, 2008) are used in our hydrogen storage simulations a brief explanation of their characteristics and structure follows. Carbon nanotubes (CNTs) are graphene sheets that have been rolled into cylindrical shapes that are typically a few nanometers in diameter. The carbon atoms that make up the sides of the tube are arranged in a hexagonal pattern.

There are three types of CNT: armchair, zigzag and chiral, depending on the orientation of the edges of the graphitic planes as they are joined to form cylinders. The chiral vector is used to specify the CNT type and is expressed in terms of the unit vectors $\vec{a}_1$ and $\vec{a}_2$, which are

![Figure 3.3](image)

**Figure 3.3** A diagram showing how different types of carbon nanotubes can be identified. The vector $\vec{C}_h$ is the chiral vector and $T$ is the tube axis (from Wikipedia, 12, Jan., 2012, public domain, Kebes author.).

 oriented along two directions within the unit hexagonal cell as illustrated in Figure 3.3. Also shown is the chiral vector, which is given by the expression

$$\vec{C}_h = m\vec{a}_1 + n\vec{a}_2$$  \hspace{1cm} (3.181)
In the case where \( m = 0 \), the resulting nanotubes are called "zigzag". When \( m = n \), the nanotubes are called "armchair". For all other cases, they are called "chiral". A chiral angle of 30 degrees separates zigzag from armchair types. The diameter of a nanotube from the center of the tube to the center of the surrounding carbon atoms is given by

\[
d = \frac{a}{\pi} \sqrt{n^2 + nm + m^2}
\]  

(3.182)

where \( a = 0.246 \) nm. Recent simulations in the literature indicate that hydrogen adsorption can be affected by CNT diameter and to a lesser extent by chirality (Cheng et al., 2005).
Chapter 4 - Theoretical Developments and Contributions to Intrinsic Quantum Thermodynamics

From its beginnings in the late 1970s and early 1980s, IQT has seen a number of significant developments. Most have concerned extensions of the theory with respect to an isolated thermodynamic system. Recently, Beretta (Beretta, 2008a; 2009a) has laid the groundwork for systems that interact with the environment by means of a heat interaction. In order to describe the system of interest with relatively few degrees of freedom interacting with an environment having innumerable or at least a continuum of degrees of freedom, Beretta found a method of incorporating classical, phenomenological relations that describe heat interactions on the macroscopic level as equations of constraint to reshape the IQT equation of motion (e.g., see Section 3.7 of Chapter 3).

In the present chapter, original contributions to the theory of IQT are proposed and discussed. First, the results of the implementation of Beretta’s work to include heat interactions within IQT are summarized. Discussed are areas where the original formulation regarding the heat interaction of Beretta has required some reinterpretation in order to allow a solution that reaches mutual stable equilibrium with the environment. A new geometrical method for extending the theory of IQT of an isolated system to include heat interactions is presented. In addition both the phenomenological technique of Beretta and geometrical transformations of the more recent development are used to extend the IQT equation of motion to include simple mass interactions of open systems for a single non-reacting chemical constituent. Lastly, the lower limit for the Beretta time functional is formulated for the heat interaction operator.

4.1 Conceptual Refinements to the QT Heat Interaction Term

As presented in Chapter 3, Beretta in (Beretta, 2009a) has developed a method for extending the IQT equation of motion to include heat interactions. During an interaction, the system of interest should seek a state of mutual stable equilibrium with an external reservoir with the system eventually reaching the same temperature as the reservoir. To simplify the derivation,
the external heat reservoir is treated phenomenologically. The reservoir is described as having a constant temperature and always in a state of stable equilibrium. Details about the reservoir such as its individual eigenvalues and probability distributions are not specified. For convenience, the resulting heat interaction operator will be referred to as the Beretta Phenomenological Heat Interaction (BPHI) operator.

Beretta (2009a) formulated the BPHI consistent with the phenomenological expression of the heat interaction which occurs between the system and reservoir, i.e.,

\[
\frac{d\langle H \rangle}{dt} = T_Q \frac{d\langle S \rangle}{dt}
\]  
(4.1)

where \( T_Q \) is in this balance equation represents the reservoir temperature \( T_R \) when

\[
\frac{d\langle S \rangle}{dt} = \frac{d\langle S \rangle_{res}}{dt} = \frac{d\langle S \rangle_{res}}{T_R} \]
(4.2)

The expression for the BPHI operator expressed in Massieu form is similar to that of the dissipation operator and appears as,

\[
\dot{\rho}_Q \equiv \text{BPHI operator} \equiv \left( \frac{1}{2\tau_G \sqrt{\langle \Delta G \Delta G \rangle}} \right) \{ \Delta G, \rho \} = \frac{1}{\tau_Q} \{ \Delta G, \rho \}
\]  
(4.3)

with

\[
\Delta G = \Delta S - \frac{H}{\theta_Q}
\]  
(4.4)

and \( \theta_Q \) which is a non-equilibrium temperature, defined as

\[
\theta_Q = \frac{\theta_S}{\theta_S - T_Q}
\]  
(4.5)

A more detailed description is given in (Beretta, 2009a) and summarized Chapter 3 of this dissertation. Although the interpretation of \( T_Q \) as \( T_R \) is consistent with the energy balance as given by equations (4.1 and 4.2). This original interpretation of \( T_Q \) as indicated in Chapter 3 does not allow the BPHI term (equation (3.170)) of the IQT equation of motion to bring the system to mutual stable equilibrium with reservoir. The following section discusses (also see section 3.7 of Chapter 3) how \( T_Q \) and the operator of equation (4.3) can be reinterpreted to overcome this problem.
4.1.1 Implementation of the BPHI: Reinterpretation of $T_Q$

As seen in Figure 4.1 a), defining $T_Q$ as the reservoir temperature $T_R$ leads to a trajectory does not move the system to a state of mutual stable equilibrium with the reservoir. The problem can be overcome if $T_Q$ is seen as a non-equilibrium temperature that is the slope of the trajectory

![Figure 4.1](image)

**Figure 4.1.** Diagram showing the trajectory of system state in the $\langle E \rangle - \langle S \rangle$ plane when a) $T_Q$ is the reservoir temperature $T_R$ and b) when $T_Q$ is the slope of the line connecting states $A_1$ and $A_0$.

in $\langle E \rangle - \langle S \rangle$ space connecting the present state of the system $A_1$ with the final state $A_0$ at mutual stable equilibrium with the reservoir. The trajectory may be linear or curved. Such an interpretation does not violate equation (4.1) if, instead of equation (4.2) we have

$$
\frac{d\langle S \rangle}{dt} = \frac{d\langle S \rangle_{sys}}{dt} = \frac{d\langle H \rangle/\langle dt \rangle}{T_R} + \dot{S}_{irrQ} = \frac{d\langle H \rangle/\langle dt \rangle}{T_Q}
$$

(4.6)

where $\dot{S}_{irrQ}$ is the entropy generation associated with the dissipative nature of the heat interaction $d\langle H \rangle/\langle dt \rangle$. In the absence of other thermodynamic effects such as spontaneous internal dissipation, the mutual equilibrium point $A_0$ serves as the only attractor of the system away from its current state. As seen in Figure 4.1 b), the path of evolution is due to the heat interaction alone appears as a linear trajectory on an $\langle E \rangle - \langle S \rangle$ diagram connecting states $A_1$ and $A_0$. Curved trajectories occur when the effects of both the reservoir and the internal dissipation term $\dot{\rho}_D$ are taken into account.

The implementation of the BPHI operator term as developed by Beretta (2009a), but under the assumption that $T_Q \neq T_R$ shows that $T_Q$ may be positive or negative depending on the circumstance. Moreover, to enable paths that move in any direction, not only must the sign of $T_Q$...
Figure 4.2 The trajectories determined from IQT simulations that use a BPHI operator that is negative with various positive and negative values for $T_Q$. The dynamics is based on a system of 5 energy eigenlevels and $\tau_Q = 1$.

Figure 4.3. The trajectories derived for a BPHI operator that is positive and with various positive and negative values for $T_Q$. The paths extend from a common initial state to the curve of stable equilibrium states with each trajectory distinguished by a differing $T_Q$ value. The range of trajectories covers the region of positive and negative temperatures on the $\langle E \rangle - \langle S \rangle$ stable
equilibrium curve. Note that the range of possible trajectories spans only 180 degrees. $T_Q$ is negative in the region between $T_Q = 0$ and a near vertical $T_Q$, in Figure 4.2 where $T_Q = -0.4$ is shown by the dashed line.

In Figure 4.3 the sign of the BPHI operator is positive. Coverage of 180 degrees for the upper part of the $\langle E \rangle - \langle S \rangle$ region is possible with $T_Q$ being both positive and negative. There are also examples where trajectories cannot move past certain limits such as the light blue curve associated with the primordial partial equilibrium (PE) states.

4.1.2 A $T_Q$ that Varies Along the Trajectory

The IQT equation of motion predicts that a thermodynamic system will exhibit internal dissipation regardless of whether it is interacting with the environment (e.g., Hatsopoulos and Gyftopoulos, 1976a,b,c,d; Beretta, 1981; Beretta 2009a,b). For a system that interacts with an external reservoir, there are two causes by which the state of a system can evolve with time. The

![Figure 4.4 Depiction of the need for reorienting $T_Q$ as the trajectory of the state of the system evolves. The internal dissipation term is included along with the BPHI term in the IQT equation of motion. The dynamics for a 5-level system and $\tau_D = 1$ and $\tau_Q = 1$.](image)

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internal dissipation operator induces the state to move horizontally in the partial equilibrium $\langle E \rangle-\langle S \rangle$ plane in a straight line towards the curve of stable equilibrium states. The heat interaction causes the state to move obliquely in a straight line toward the point of mutual stable equilibrium with the reservoir. The two influences result in a curved trajectory as the system evolves. The quantity $T_Q$ represents the slope at any point along the curved trajectory. In order for the equation of motion to follow this curved path, a quantity denoted as the linear slope, $T_Q(l)$, between the present state and the final state of the system in mutual stable equilibrium with the reservoir, must be updated at each time step in the algorithm. Figure 4.4 shows a red, curved trajectory produced by updating $T_Q(l)$. In addition the green line represents the heat interaction term alone, while the light blue line represents the internal dissipation term alone. The violet colored line is the case where both heat and dissipation effects are present but $T_Q(l)$ is not updated.

4.1.3 Difficulties in Implementing the BPHI: Singularities

The expression for $\theta_Q$ in equation (4.5) is seen to become singular whenever $\theta_S$ and $T_Q$ have the same value. At such points, the heat interaction operator makes a sign change that must be accounted for if the solution for the heat interaction is to be calculated all the way to equilib-

![Figure 4.5](image)

**Figure 4.5** An example depicting a singularity in $\theta_Q$ for the BPHI operator, encountered as the state of the system evolves with time. The dynamics are for a 20-level system and $\tau_0 = 33.3$ and $\tau_Q = 10$ and $T_R = 0.041$. 

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**Figure 4.6.** \( \langle E \rangle - \langle S \rangle \) trajectories showing the locations of singularities for the case with the BPHI term only (Q only) and for the case with the BPHI term and the interaction plus internal dissipation (D+Q) term. The dynamics is for a 20-level system and \( \tau_D = 33.3 \) and \( \tau_Q = 10 \) and \( T_R = 0.041 \).

**Figure 4.7.** A diagram showing the inflection points of the occupation probability trajectories for the state matrix \( \rho \) that are associated with singularities. Included are the BPHI term alone (Q only) and the BPHI term plus the internal dissipation term (D+Q). The dynamics is for a 20-level system and \( \tau_D = 33.3 \) and \( \tau_Q = 10 \) and \( T_R = 0.041 \).
The singularities correspond to inflection points in the state operator trajectories where the slopes of the trajectories become nearly vertical. By perturbing the system beyond the inflection point and changing the sign of the BPHI operator, implementations of the BPHI term are able to continue to stable equilibrium. Figure 4.5 is a graph of $\theta_S$, $\theta_H$, $\theta_Q$ and $T_R$ with time showing an example of a singularity where $\theta_Q$ becomes infinite. Figure 4.6 depicts a $\langle E \rangle - \langle S \rangle$ trajectory for a heat BPHI alone and one where the dissipation term and BHPI term are included. The locations of the singularities are marked in blue.

Figure 4.7 shows the corresponding evolution of the state operator for the two cases in Figure 4.6. The traces for each case become nearly vertical at the singular points, which for the BPHI term alone is near time $t = 5$ and for the BPHI term and dissipation terms near time $t = 10$. Each example has 20 energy eigenlevels. A linear interpolation of the state operator trajectories past the singular points along with a sign change for $T_{Q(l)}$ is made to allow the solution algorithm

![Figure 4.8](image)

**Figure 4.8** Example of inflection points and tight curvature associated with singularities encountered with the BPHI operator. Depicted are the effects of the BPHI term plus the dissipation term. The problem area is seen to be around $t = 420$. The dynamics is for a 20-level system and $\tau_0 = 1.0$ and $\tau_Q = 10$ and $T_R = 0.041$.  

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to complete the trajectories to stable equilibrium.

In another example, Figure 4.8 shows abrupt curvature in the state operator evolution when the strength of the heat interaction effect as given by its $\tau$ value is greater than about ten times that for the internal dissipation. Even though it is possible to deal with the encountered singularities, their presence and the tight curvature of the occupation probabilities near them indicate that the singularities are likely an artifact of the formulation of the BPHI operator and not of physical significance.

Besides the singularities, another concern that is not resolved in Beretta (2009a) is the type of optimal path a heat interaction takes. For internal dissipation, the system trajectory takes the path of steepest entropy ascent. It is not clear whether the evolution of the BPHI term coincides with a path of steepest entropy ascent, steepest energy ascent/descent or a combination of both. In an attempt to circumvent these issues, an alternative formulation of the BPHI operator has been developed that is based on rotation of the IQT internal dissipation operator.

### 4.2 Heat Interaction Operator by Rotational Transform of the Dissipation Operator

As equation (4.6) implies, the BPHI operator with the choice of $T_0 \neq T_R$ actually represents both a heat interaction with entropy generation and entropy transfer across the system boundary plus entropy generation due to internal dissipation. To capture all of these effects and eliminate the drawbacks to the BPHI outlined in the previous section, the alternative operator proposed here starts with the internal dissipation operator and rotates it in the $\langle E \rangle - \langle S \rangle$ plane by means of a rotation matrix. The rotation amounts to a unitary transformation of the Beretta dissipation operator with the angle of rotation determined by the current and final state of the system. Unlike the BPHI term, the equation of motion now produces a trajectory which follows a path of steepest entropy ascent, albeit in the rotated space. The transformation is straightforward and yields results that are similar to the BPHI operator with $T_0 \neq T_R$ while avoiding the $\theta_Q$ singularities and other difficulties discussed above. The new rotationally derived operator for convenience is called the Rotated Phenomenological Heat Interaction (RPHI) operator. Details of the derivation are shown below.
The Massieu (or Helmholtz) form of a dissipation operator is transformed to a new rotated space. The rotated quantities are shown with tildes. Thus instead of $G$, $S$ and $H$,

$$\tilde{G}(\tilde{H},\tilde{S}) = \tilde{S} - \frac{\tilde{H}}{\tilde{\theta}_H}$$  \hspace{1cm} (4.7)

For a rotation to make sense, the $H$ and $S$ axes need to have the same units. A diagonal scaling matrix can be applied such that

$$\begin{bmatrix} S \\ H/T^* \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1/T^* \end{bmatrix} \begin{bmatrix} S \\ H \end{bmatrix}$$  \hspace{1cm} (4.8)

where $T^*$ has the units of temperature and a magnitude of unity. The inverse of the scaling matrix is applied after the rotation to restore the units of energy and entropy to the transformed coordinate system. The scaling matrix otherwise has no further effect on the calculations. Together with the rotation matrix, the full transformation to the new variable space is then

$$\begin{bmatrix} \tilde{S} \\ \tilde{H} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & T^* \end{bmatrix} \begin{bmatrix} \cos \varphi & -\sin \varphi \\ \sin \varphi & \cos \varphi \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & 1/T^* \end{bmatrix} \begin{bmatrix} S \\ H \end{bmatrix}$$  \hspace{1cm} (4.9)

which results in

$$\tilde{S} = S \cos \varphi - (H/T^*) \sin \varphi$$  \hspace{1cm} (4.10)

$$\tilde{H} = ST^* \sin \varphi + H \cos \varphi$$  \hspace{1cm} (4.11)

The angle $\varphi$ is related to the slope of the heat interaction trajectory through the relation

$$\varphi = \tan^{-1} \frac{T_Q}{T^*}$$  \hspace{1cm} (4.12)

As depicted in Figure 4.9, by applying the rotation matrix, the horizontal path for a dissipation operator in the $H$-$S$ plane is transformed into a slanted path that is characteristic of a heat interaction operator. The angle of rotation is $\varphi$, which gives the transformed entropy operator axis $\tilde{S}$ a linear slope $T_{Q(l)}$ with respect to the original coordinate system. The rotation makes the RPHI operator a function of both the energy and entropy operators of the original space. Instead of $S$ following a steepest path with $H$ being held constant, the state of the system now follows a steepest path with respect the transformed entropy operator, $\tilde{S}$, keeping the transformed energy operator $\tilde{H}$ a constant. Although the linear slope $T_{Q(l)}$ figures into the transformation through $\varphi$, there is no need for $\tilde{\theta}_Q$ to be constructed, only the quantity $\tilde{\theta}_H$ if the Massieu form of the dissipation operator is used or $\tilde{\theta}_S$ if the Helmholtz form is used.
The quantities $\tilde{\theta}_H$, $\tilde{\theta}_S$, $\langle \Delta \tilde{H} \Delta \tilde{H} \rangle$, $\langle \Delta \tilde{H} \Delta \tilde{S} \rangle$, etc. are derived the same way as shown in Beretta (2009a) and sections 3.5 - 3.7 of Chapter 3, the only difference being that the operators $H$ and $S$ are replaced with the transformed operators $\tilde{H}$, $\tilde{S}$ in equation (4.7) above. Once determined, the new Helmholtz (or Massieu) function is incorporated into the IQT equation of motion which is solved to yield the time evolution of the state matrix. The IQT equation of motion with both the dissipation effects and heat interaction is written as

$$\frac{d\rho}{dt} = -\frac{1}{\tau_D} \{\Delta G, \rho\} - \frac{1}{\tau_Q} \{\Delta \tilde{G}, \rho\}$$

(4.13)

with $\tau_Q$ being the relaxation constant for the heat interaction operator and $\tau_D$ for the internal dissipation operator.

Now, to put this derivation of the RPHI operator in the same geometric context described relative to the dissipation operator in Section 3.4 of Chapter 3, consider the vectors and linear manifolds depicted in Figure (4.10). In this figure, the original linear manifold $L(g_0, g_1)$ used in the derivation of the dissipation operator is shown as is that associated with the RPHI operator in the rotated coordinated space, i.e., $\tilde{L}(\tilde{g}_0, \tilde{g}_1)$. Also, seen in this figure are the $b$ and $\tilde{b}$ vectors and their parallel and perpendicular components $b_L$, $\tilde{b}_L$, $b_\perp$, and $\tilde{b}_\perp$. Recalling equations (3.116) to (3.118) one can write that

$$\gamma = \gamma_D = b - b_L = b_\perp$$

(4.14)
In a similar vein, one can express the equation of motion with the RPHI operator only as
\[ \dot{\gamma} = \dot{\gamma}_Q = b - b_L = b_\perp \] (4.15)
In the case of equation (4.14) \( b_\perp \) represents the path of steepest entropy ascent, while in equation (4.15) \( \tilde{b}_\perp \) the path of steepest entropy ascent. Obviously, these representations for \( b_\perp \) and \( \tilde{b}_\perp \) are based on different linear manifold, namely \( L(g_0, g_1) \) and \( \tilde{L}(\tilde{g}_0, \tilde{g}_1) \), respectively. However, if instead one were to represent equation (4.15) relative to \( L(g_0, g_1) \) as opposed to \( \tilde{L}(\tilde{g}_0, \tilde{g}_1) \), one could conclude that the path followed is \( b'_\perp \) as seen in Figure 4.10 and, thus,
\[ \dot{\gamma} = \dot{\gamma}_Q = b - b'_L = b'_\perp \] (4.16)

**Figure 4.10** Depiction of the geometric construction of the dissipation and RPHI operators

Furthermore, if one represents \( \tilde{b} \) in terms of the operators \( S \) and \( H \) and not \( \tilde{S} \) and \( \tilde{H} \) i.e.,
\[ \tilde{b} = \frac{\partial \langle S \rangle}{\partial \gamma} = \text{Tr} \left( \gamma^+ \left( S \cos \phi - \frac{H}{T^*} \sin \phi \right) \right) \] (4.17)
It is evident that both \( S \) and \( H/T^* \) contribute to \( \tilde{b} \) with the former associated with the dissipation which occurs when the entropy is transferred to or from the system and the latter with the actual transfer of entropy itself. Subtracting off \( b'_L \) which is the projection of \( \tilde{b} \) onto the linear manifold \( L(g_0, g_1) \) one is left with \( b'_\perp \) which follows a path of steepest entropy ascent but at the expense of violating the \( g_1 \) constraint. The violation however is compensated by the fact that the length of the \( b'_\perp \) varies in proportion to the change in entropy associated with the change in energy due to the interaction of the system with the heat reservoir. One can conclude that \( b'_\perp \) no longer simply represents the path of steepest entropy ascent but also one of steepest energy ascent or descent.
4.3 Derivation of the Mass Interaction Operator

The Beretta formalism can be extended to include mass interactions. A mass interaction is an interaction between the thermodynamic system of interest and a mass reservoir such that energy, entropy and mass are able to cross the system boundary. The following lays out two methods for the derivation of a simple mass interaction operator. The first is along the lines of the phenomenological approach of Beretta (2009a) for the heat interaction presented in Chapter 3, while the other uses a rotational transform of the dissipation operator in three dimensions. Before either method can be applied, the dissipation operator for an open system allowing mass flow across the boundary must be developed.

4.3.1 Derivation of the Dissipation Operator for an Open System

To accommodate changes in particle number $n$ of a single atomic species, a number density operator or generator of the motion, $N$, must be included in the formulation of the dissipation operator of Beretta as shown in the following equation where it is assumed that $\rho$ is diagonal in the Hamiltonian representation:

$$
D_j = -\frac{1}{\tau_M} \begin{vmatrix}
\rho_j \ln \rho_j & \rho_j & \rho_j e_j & \rho_j n_j \\
\sum \rho_i \ln \rho_i & 1 & \sum \rho_i e_i & \sum \rho_i n_i \\
\sum \rho_i \ln \rho_i e_i & \sum \rho_i e_i & \sum \rho_i e_i^2 & \sum \rho_i n_i e_i \\
\sum \rho_i \ln \rho_i n_i & \sum \rho_i n_i & \sum \rho_i n_i e_i & \sum \rho_i n_i^2 \\
\end{vmatrix}
$$

(4.18)

The symbol $D_j$ represents the $j^{th}$ element of the dissipation operator and $\tau_M$ is a time functional that scales the rate of internal relaxation for the system. The $n_i$ indicate the number of particles that have energy eigenvalue $e_i$ within the system. The expectation value for the number of particles in the system is given by

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\[ \langle N \rangle = \sum_i \rho_i n_i \]  

(4.19)

In addition, the expectation value for the system energy is

\[ \langle H \rangle = \sum_i \rho_i e_i \]  

(4.20)

and for the entropy

\[ \langle S' \rangle = -k_b \sum_i \rho_i \ln \rho_i \]  

(4.21)

The determinants of equation (4.12) can be rewritten in the notation of Beretta (2009a) as

\[
S'_{\perp L(\gamma, H', N')} = \begin{vmatrix}
S' & \gamma & H' & N' \\
S' \cdot \gamma & \gamma \cdot \gamma & H' \cdot \gamma & N' \cdot \gamma \\
S' \cdot H' & \gamma \cdot H' & H' \cdot H' & N' \cdot H' \\
S' \cdot N' & \gamma \cdot N' & H' \cdot N' & N' \cdot N'
\end{vmatrix}
\]

(4.22)

where

\[ H' = 2\gamma H \]  

(4.23)

\[ S' = 2\gamma S \]  

(4.24)

\[ N' = 2\gamma N \]  

(4.25)

The quantity \( S'_{\perp L(\gamma, H', N')} \) is the component of the entropy vector \( S' \) that is perpendicular to the linear manifold \( L \) which contains the generators of the motion. The vector \( \gamma \) has been substituted for the density operator \( \rho \) according to the relation

\[ \rho = \langle \gamma \rangle \langle \gamma \rangle^\dagger = \gamma \gamma^\dagger \]  

(4.26)

The use of \( \gamma \) ensures that solutions to the Beretta equation are non-negative definite.

A row interchange and a column interchange can be performed on the upper and lower determinants of equation (4.22), so that the terms containing \( \gamma \) are in the top row and leftmost column. The two interchanges leave the value of equation (4.22) unaffected. By applying the Chió Pivotal Concentration method (Chió, 1853; and, e.g., Weisstein, 2011) and noting that \( \gamma \cdot \gamma \) is equal to unity, the dimensions of the determinants in equation (4.22) can be reduced, resulting in
\[ S'_{\perp L(\gamma, H', N')} = \begin{vmatrix} (\Delta S)' & (\Delta H)' & (\Delta N)' \\ (\Delta S)' \cdot (\Delta S)' & (\Delta H)' \cdot (\Delta H)' & (\Delta N)' \cdot (\Delta H)' \\ (\Delta S)' \cdot (\Delta N)' & (\Delta H)' \cdot (\Delta N)' & (\Delta N)' \cdot (\Delta N)' \end{vmatrix} \]

(4.27)

with

\[(\Delta H)' = 2\gamma \Delta H\]

(4.28)

\[(\Delta S)' = 2\gamma \Delta S\]

(4.29)

\[(\Delta N)' = 2\gamma \Delta N\]

(4.30)

Expanding the determinants gets,

\[ S'_{\perp L(\gamma, H', N')} = (\Delta S)' + \frac{[(\Delta H)' \cdot (\Delta N)' \cdot (\Delta S)' \cdot (\Delta N)' - (\Delta H)' \cdot (\Delta S)' \cdot (\Delta N)' \cdot (\Delta N)'] (\Delta H)'}{(\Delta H)' \cdot (\Delta H)' \cdot (\Delta N)' \cdot (\Delta N)' - (\Delta H)' \cdot (\Delta N)' \cdot (\Delta H)' \cdot (\Delta N)'} + \frac{[(\Delta H)' \cdot (\Delta S)' \cdot (\Delta H)' \cdot (\Delta N)' - (\Delta H)' \cdot (\Delta S)' \cdot (\Delta N)' \cdot (\Delta N)'] (\Delta N)'}{(\Delta H)' \cdot (\Delta H)' \cdot (\Delta N)' \cdot (\Delta N)' - (\Delta H)' \cdot (\Delta N)' \cdot (\Delta H)' \cdot (\Delta N)'} \]

(4.31)

Making use of the fact that \((\Delta A) \cdot (\Delta B)\) is a covariance given by

\[(\Delta A)' \cdot (\Delta B)' = \langle AB \rangle - \langle A \rangle \langle B \rangle \equiv \langle AA \rangle \langle BB \rangle\]

(4.32)

equation (4.31) can be rewritten in terms of variances and covariances such that

\[ S'_{\perp L(\gamma, H', N')} = (\Delta S)' + \frac{\langle \Delta H \Delta N \rangle \langle \Delta S \Delta N \rangle - \langle \Delta H \Delta S \rangle \langle \Delta N \Delta N \rangle}{\langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle - \langle \Delta H \Delta N \rangle \langle \Delta H \Delta N \rangle} \langle \Delta H \rangle' \]

\[ + \frac{\langle \Delta H \Delta S \rangle \langle \Delta H \Delta N \rangle - \langle \Delta H \Delta H \rangle \langle \Delta S \Delta N \rangle}{\langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle - \langle \Delta H \Delta N \rangle \langle \Delta H \Delta N \rangle} \langle \Delta N \rangle' \]

(4.33)

A pair of non-equilibrium enthalpies may be defined as

\[ h_H = \frac{\langle \Delta H \Delta H \rangle}{\langle \Delta H \Delta N \rangle} \]

(4.34)

\[ h_N = \frac{\langle \Delta H \Delta N \rangle}{\langle \Delta N \Delta N \rangle} \]

(4.35)

The covariance \(\langle \Delta H \Delta N \rangle\) then can therefore be expressed as

\[ \langle \Delta H \Delta N \rangle = \frac{1}{h_H} \langle \Delta H \Delta H \rangle = h_N \langle \Delta N \Delta N \rangle \]

(4.36)

which allows the denominator of equation (4.33) to be simplified to

\[ \langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle - \langle \Delta H \Delta N \rangle \langle \Delta H \Delta N \rangle = \langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle \left(1 - \frac{h_N}{h_H}\right) \]

(4.37)
Making the substitution $A = \left(1 - \frac{h_N}{h_H}\right)$ and separating the terms, equation (4.33) becomes

$$S'_{\perp L(\gamma,H',N')} = (\Delta S) + \left\{ \frac{\langle \Delta H \Delta N \rangle \langle \Delta S \Delta N \rangle - \langle \Delta H \Delta S \rangle \langle \Delta N \Delta N \rangle}{A \langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle} \right\} (\Delta H)' + $$

$$\left\{ \frac{\langle \Delta H \Delta S \rangle \langle \Delta H \Delta N \rangle - \langle \Delta H \Delta H \rangle \langle \Delta S \Delta N \rangle}{A \langle \Delta H \Delta H \rangle \langle \Delta N \Delta N \rangle} \right\} (\Delta N)' (4.38)$$

New non-equilibrium parameters can now be defined such that

$$\theta_H = \frac{\langle \Delta H \Delta H \rangle}{\langle \Delta H \Delta S \rangle} \tag{4.39}$$

$$s_N = \frac{\langle \Delta S \Delta N \rangle}{\langle \Delta N \Delta N \rangle} \tag{4.40}$$

and with these, equation (4.38) is rewritten as

$$S'_{\perp L(\gamma,H',N')} = (\Delta S) + \frac{1}{A} \left\{ \frac{s_N}{h_H} - \frac{1}{\theta_H} \right\} (\Delta H)' + \frac{1}{A} \left\{ \frac{h_N}{\theta_H} - s_N \right\} (\Delta N)' \tag{4.41}$$

The conversion of equation (4.41) back to a form based on $\rho$ instead of $\gamma$, and the inclusion of the time functional $\tau$, produces the dissipation operator $D$ for a system having constant energy but with a varying number of particles of a single species. The form has the desired Massieu function structure, namely,

$$D = \frac{1}{\tau_D} \{ \Delta M, \rho \} \tag{4.42}$$

with the Massieu function $M$ given by

$$M(H,S,N) = S - \frac{h_H}{(h_H - h_N)} \left( \frac{1}{\theta_H} - \frac{s_N}{h_H} \right) H + \frac{h_H}{(h_H - h_N)} \left( \frac{h_N}{\theta_H} - s_N \right) N \tag{4.43}$$

and

$$\Delta M = \Delta S - \frac{h_H}{(h_H - h_N)} \left( \frac{1}{\theta_H} - \frac{s_N}{h_H} \right) \Delta H + \frac{h_H}{(h_H - h_N)} \left( \frac{h_N}{\theta_H} - s_N \right) \Delta N \tag{4.44}$$

The dissipation operator can now be used as a template for constructing the mass interaction operator based on Beretta’s phenomenological approach,

$$\dot{\rho}_D = \frac{1}{\tau_D} \{ \Delta G, \rho \} \tag{4.45}$$

with $\Delta G$ having the form of a Massieu-like function.
4.3.2 Derivation of the Mass Interaction Operator based on Beretta’s Phenomenological Approach

Equation (4.44) can serve as a starting point for deriving a mass interaction operator. The general structure of $\Delta G$ is the same as $\Delta M$ in the dissipation operator but with differing parameters that are yet to be determined, namely,

$$
\Delta G = \Delta S - \left( \frac{1}{\theta} - \frac{s}{h} \right) \Delta H + \left( \frac{h}{\theta} - \frac{s}{h} \right) \Delta N
$$

(4.46)

The objective is to find the quantities $\theta, s, h$ in terms of the variances and covariances of the operators $H, S$ and $N$, that is, the parameters $\theta_H, \theta_S, h_H, h_N, s_S, s_N$ while at the same time obeying the constraints imposed by the phenomenological mass interaction balance equations.

For convenience, in equation (4.46), let

$$
B = \left( \frac{1}{\theta} - \frac{s}{h} \right)
$$

(4.47)

and

$$
hB = \left( \frac{h}{\theta} - \frac{s}{h} \right)
$$

(4.48)

The resulting expression for $\Delta G$ is,

$$
\Delta G = \Delta S - B \Delta H + hB \Delta N
$$

(4.49)

To solve for $B$ and $h$, the mass interaction balance equations (i.e., for mass, energy, and entropy) are written for the system interacting with a mass reservoir in terms of the expectation values $\langle N \rangle, \langle H \rangle$ and $\langle S \rangle$ for the system. Thus,

$$
\frac{d\langle N \rangle}{dt} = \text{particle flow rate}
$$

(4.50)

$$
\frac{d\langle H \rangle}{dt} = h_{MR} \frac{d\langle N \rangle}{dt}
$$

(4.51)

$$
\frac{d\langle S \rangle}{dt} = s_{MR} \frac{d\langle N \rangle}{dt} + \dot{s}_{irrm}
$$

(4.52)

where $h_{MR}$ and $s_{MR}$ are the specific enthalpy and entropy per particle of the mass which crosses the system boundary into the mass reservoir and $\dot{s}_{irrm}$ is the rate of entropy generation within the system relative to this mass interaction. Now, in a fashion analogous to what was

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done in the derivation of the BPHI operator and the choice of $T_Q \neq T_R$, the following definitions are made:

$$h_M = \frac{d\langle H \rangle / dt}{d\langle N \rangle / dt}$$  \hspace{1cm} (4.53)

$$s_M = \frac{d\langle S \rangle / dt}{d\langle N \rangle / dt}$$  \hspace{1cm} (4.54)

Analogous to the role $T_Q \neq T_R$ plays in bringing the system to a state of mutual stable equilibrium with the heat reservoir, both $h_M$ and $s_M$ play a similar role in providing a path through $\langle E \rangle - \langle S \rangle - \langle N \rangle$ space which the system travels from its initial state to its final state of mutual stable equilibrium with the mass reservoir. This path describes an irreversible process with the associated changes to the eigenvalues of the state matrix $\rho$ being non-unitary.

The time derivatives of the expectation values are defined in terms of traces. As shown previously in Chapter 3,

$$\frac{d\langle H \rangle}{dt} = \text{Tr} \dot{\rho} H = \text{Tr} \dot{\rho} \Delta H$$  \hspace{1cm} (4.55)

$$\frac{d\langle S \rangle}{dt} = \text{Tr} \dot{\rho} S = \text{Tr} \dot{\rho} \Delta S$$  \hspace{1cm} (4.56)

$$\frac{d\langle N \rangle}{dt} = \text{Tr} \dot{\rho} N = \text{Tr} \dot{\rho} \Delta N$$  \hspace{1cm} (4.57)

For the mass interaction by itself without the contribution of internal dissipation term, the time derivative of the state operator takes the form,

$$\dot{\rho} = \frac{1}{2} \left( \frac{1}{\tau_M} \right) \{ \Delta G, \rho \}$$  \hspace{1cm} (4.58)

The term in parentheses containing $\tau_M$ is $1/\tau$, a time functional of $\rho$ that is calculated separately using the Heisenberg time-energy (see Section 4.4 below for an analogous derivation for $\tau_M$) uncertainty relation and does not affect the current derivation. Let us define,

$$\frac{1}{\tau} = \frac{1}{\tau(\rho)} \equiv \left( \frac{1}{\tau_M} \right) \left( \frac{1}{\sqrt{\langle \Delta G \Delta G \rangle}} \right)$$  \hspace{1cm} (4.59)

Equation (4.55) can be written as

$$\frac{d\langle H \rangle}{dt} = \text{Tr} \dot{\rho} \Delta H = \frac{1}{2\tau} \text{Tr} \{ \Delta G, \rho \} \Delta H$$  \hspace{1cm} (4.60)
with $1/\tau$ taken out of the trace since it is a scalar quantity. The anti-commutator term in equation (4.60) is rearranged using the cycling property of the trace to find
\[
\frac{1}{2} \text{Tr}[\Delta G, \rho] \Delta H = \frac{1}{2} \text{Tr}(\Delta G \rho + \rho \Delta G) \Delta H = \frac{1}{2} \langle \Delta H \Delta G \rangle + \frac{1}{2} \langle \Delta G \Delta H \rangle = \langle \Delta H \Delta G \rangle
\] (4.61)
Using equation (4.45), the Massieu form for equation (4.57) can be obtained, i.e.,
\[
\langle \Delta H \Delta G \rangle = \langle \Delta H \Delta S \rangle - B \langle \Delta H \Delta H \rangle + hB \langle \Delta H \Delta N \rangle
\] (4.62)
and as a result,
\[
\frac{d\langle H \rangle}{dt} = \frac{1}{\tau} \left( \langle \Delta H \Delta S \rangle - B \langle \Delta H \Delta H \rangle + hB \langle \Delta H \Delta N \rangle \right)
\] (4.63)
Taking note from equations (4.34) and (4.39) that $\langle \Delta H \Delta S \rangle = \langle \Delta H \Delta H \rangle / \theta_H$ and $\langle \Delta H \Delta N \rangle = \langle \Delta H \Delta H \rangle / h_H$, equation (4.63) can be rewritten as
\[
\frac{d\langle H \rangle}{dt} = \frac{1}{\tau} \left( \frac{1}{\theta_H} - B + \frac{hB}{h_H} \right) \langle \Delta H \Delta H \rangle
\] (4.64)
Starting from equations (4.56) and (4.57) a similar expressions for $d\langle S \rangle/dt$ and $d\langle N \rangle/dt$ can be obtained,
\[
\frac{d\langle S \rangle}{dt} = \frac{1}{\tau} \left( 1 - \theta_S B + \frac{hB}{s_S} \right) \langle \Delta S \Delta S \rangle
\] (4.65)
and
\[
\frac{d\langle N \rangle}{dt} = \frac{1}{\tau} \left( s_N - h_N B + hB \right) \langle \Delta N \Delta N \rangle
\] (4.66)
where
\[
\theta_S = \frac{\langle \Delta H \Delta S \rangle}{\langle \Delta S \Delta S \rangle}
\] (4.67)
\[
s_S = \frac{\langle \Delta S \Delta S \rangle}{\langle \Delta N \Delta S \rangle}
\] (4.68)
\[
h_N = \frac{\langle \Delta H \Delta N \rangle}{\langle \Delta N \Delta N \rangle}
\] (4.69)
\[
s_N = \frac{\langle \Delta S \Delta N \rangle}{\langle \Delta N \Delta N \rangle}
\] (4.70)
Now substituting equations (4.64), (4.65) and (4.66) into equations (4.53) and (4.54) allows $h$ and $B$ to be determined in terms of the parameters $\theta_H, \theta_S, h_H, h_N, h_M, s_S, s_N$ and $s_M$. It
should be noted that $s_M$ and $h_M$ are kinematic parameters that are set independently of the others to allow the system follow the correct path in $\langle E \rangle - \langle S \rangle - \langle N \rangle$ space. In the absence of the dissipation operator, the trajectory of the state of the system for the mass interaction operator is a straight line from the initial state to the final state of the system in mutual stable equilibrium with the mass reservoir. Solving for $B$ and $h$ results in

$$B = \frac{\theta_H \left( s_N - s_s s_N / s_M \right) \left( h_M - h_N \right) + \left( 1 + s_N / s_M \right) \left( h_H h_N - \theta_H s_N h_M \right)}{\theta_H \left( \mu_N - s_s s_N \theta_s / s_M \right) \left( h_M - h_N \right) - \left( 1 + s_N / s_M \right) \left( h_M h_N - h_H h_N \right)}$$

(4.71)

and $h$ is,

$$h = \frac{\left( h_H h_N - \theta_H s_N h_M \right) + \left( h_M h_N - h_H h_N \right) B}{\theta_H \left( h_M - h_N \right)}$$

(4.72)

By letting $s_M \rightarrow 0$ and $h_M \rightarrow 0$, $B$ and $h$ are seen to converge as expected to the corresponding versions of these parameters for $\Delta M$ in equation (4.44) with the factor $h_H / (h_H - h_N)$ included.

### 4.3.3 Derivation of the Mass Interaction Operator via a Rotation Matrix

Unfortunately, the phenomenological mass interaction (PMI) operator just derived comes with similar drawbacks to the ones enumerated with the BPHI operator. To circumvent these difficulties the same approach as used to derive the RPHI operator is used, i.e., rotation matrices. The rotations transform the dissipation operator which is based on steepest entropy ascent at constant energy and particle number into an operator which allows the energy and number of particles to vary. In a 3-dimensional space of $\langle H \rangle - \langle S \rangle - \langle N \rangle$, two rotations are necessary. A first rotation in azimuth defined about the $N$ axis is

$$\begin{bmatrix} \hat{S} \\ \hat{s} \hat{H} / h^* \\ \hat{s}^* \hat{N} \end{bmatrix} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & s^* / h^* & 0 \\ 0 & 0 & s^* \end{bmatrix} \begin{bmatrix} S \\ H \\ N \end{bmatrix}$$

(4.73)

A second rotation in elevation about the $\tilde{H}$ axis that completes the transformation is

$$\begin{bmatrix} \tilde{S} \\ \tilde{s} \tilde{H} / h^* \\ \tilde{s}^* \tilde{N} \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & h^* / s^* & 0 \\ 0 & 0 & 1 / s^* \end{bmatrix} \begin{bmatrix} \cos \varphi & 0 & -\sin \varphi \\ 0 & 1 & 0 \\ \sin \varphi & 0 & \cos \varphi \end{bmatrix} \begin{bmatrix} \tilde{S} \\ s^* \tilde{H} / h^* \\ s^* \tilde{N} \end{bmatrix}$$

(4.74)

where
\[
\cos \theta(t) = \frac{\langle S_{eq} \rangle - \langle S(t) \rangle}{\sqrt{\langle S_{eq} \rangle^2 - \langle S(t) \rangle^2 + \langle H_{eq} \rangle^2 - \langle H(t) \rangle^2}} \tag{4.75}
\]

and

\[
\sin \theta(t) = \frac{\langle H_{eq} \rangle - \langle H(t) \rangle \langle s^* / h^* \rangle}{\sqrt{\langle S_{eq} \rangle^2 - \langle S(t) \rangle^2 + \langle H_{eq} \rangle^2 - \langle H(t) \rangle^2 \langle s^* / h^* \rangle^2}} \tag{4.76}
\]

while

\[
\cos \phi(t) = \frac{\langle N_{eq} \rangle - \langle N(t) \rangle \langle s^* \rangle}{\sqrt{\langle S_{eq} \rangle^2 - \langle S(t) \rangle^2 + \langle H_{eq} \rangle^2 - \langle H(t) \rangle^2 \langle s^* / h^* \rangle^2 \langle N_{eq} \rangle^2 - \langle N(t) \rangle^2 \langle s^* \rangle^2}} \tag{4.77}
\]

and

\[
\sin \phi(t) = \frac{\langle N_{eq} \rangle - \langle N(t) \rangle \langle s^* \rangle}{\sqrt{\langle S_{eq} \rangle^2 - \langle S(t) \rangle^2 + \langle H_{eq} \rangle^2 - \langle H(t) \rangle^2 \langle s^* / h^* \rangle^2 \langle N_{eq} \rangle^2 - \langle N(t) \rangle^2 \langle s^* \rangle^2}} \tag{4.78}
\]

The diagonal scaling matrix in the form of

\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & s^* / h^* & 0 \\
0 & 0 & s^*
\end{bmatrix} \tag{4.79}
\]

along with its inverse is applied to ensure the correct units are obtained for the transformations.

**Figure 4.11** Diagram of a rotationally transformed operator space for the RPMI operator. The $H$, $S$, $N$ operators are first rotated in the $H$-$S$ plane and then with respect to the $N$ axis so that the evolutionary path has constant rotated energy $\tilde{H}$ and rotated particle number $\tilde{N}$ with respect to the transformed space.
As with scaling matrix used for the RPHI, the magnitudes of the diagonal elements are unity, i.e. $h^*$ has a magnitude of one with units of specific energy while $s^*$ likewise has a magnitude of one with units of specific entropy. A schematic of the rotations is shown in Figure 4.11.

As a result of the rotations, the RPMI operator becomes

$$\dot{\rho}_M = \frac{1}{\tau} \{\Delta G, \rho\} \quad (4.80)$$

where

$$\Delta G = \Delta \tilde{S} = \frac{h_{H_{rot}}}{(h_{H_{rot}} - \mu_{N_{rot}})} \left( \frac{1}{\theta_{H_{rot}}} - \frac{s_{N_{rot}}}{h_{H_{rot}}} \right) \Delta \tilde{H}$$

$$+ \frac{h_{H_{rot}}}{(h_{H_{rot}} - h_{N_{rot}})} \left( \frac{h_{N_{rot}}}{\theta_{H_{rot}}} - s_{N_{rot}} \right) \Delta \tilde{N} \quad (4.81)$$

and

$$h_{H_{rot}} = \frac{\langle \Delta H \Delta H \rangle_{rot}}{\langle \Delta H \Delta N \rangle_{rot}} = \left\{ \frac{\text{Tr}(\rho \tilde{H}^2) - \left(\text{Tr}(\rho \tilde{H})\right)^2}{\text{Tr}(\rho \tilde{N}) - \text{Tr}(\rho \tilde{H})} \text{Tr}(\rho \tilde{N}) \right\} \quad (4.82)$$

Besides its simplicity of derivation, the RPMI operator is based on a steepest path of the transformed entropy $\tilde{S}$ in the rotated space. The straight line trajectory from initial state to final equilibrium point takes a steepest path based on all three operators $H, S$ and $N$ and not of $S$ alone. Even though the RPMI operator is based on a phenomenological description, it can be argued in a similar fashion to what was done for the RPHI operator (see the discussion surrounding Figure 4.11) that the actual path followed by the state of the system in the original untransformed space is one of steepest entropy ascent and both steepest energy and mass ascent/descent.

Explicitly, the IQT equation of motion with this new RPMI operator for a single constituent is written as

$$\dot{\rho} = -\frac{i}{\hbar} \left[ H, \rho \right] + \left\{ \frac{1}{2\tau_D \sqrt{\langle \Delta M \Delta M \rangle}}, \{\Delta M, \rho\} \right\} + \left\{ \frac{1}{2\tau_M \sqrt{\langle \Delta G \Delta G \rangle}}, \{\Delta G, \rho\} \right\} \quad (4.83)$$

The first term on the right-hand side of equation (4.83) represents the time-dependent Schrödinger term, the second is the internal dissipation operator and the last is the RPMI operator that models the irreversible exchange of mass between the system and mass reservoir.
Finally, it is possible to recast the mass RPMI operator in terms of a Helmholtz function $\Delta F$ such that

$$\Delta F = \Delta H - \frac{\Delta S}{B} - s \Delta N \quad (4.84)$$

The Helmholtz forms for $\Delta M$ and $\Delta G$ can be substituted into equation (4.83) and will produce the same dynamic result as the Massieu version.

### 4.4 Formulation of the IQT Time Constant for Heat Interactions

The formulation of the Beretta equation for an isolated system as shown in, e.g., Beretta (1981), Beretta (1984) and Beretta (2009a) requires the introduction of a quantity $\tau$ that has units of time and is used as a scaling factor for the dissipation operator. The value for $\tau$ is not as yet derivable from first principles but has the physical effect of determining the strength of the dissipation operator. The greater the magnitude of $\tau$, the longer the relaxation time for the system and the weaker the dissipation effect. For convenience, $\tau$ is often assumed to be a constant but may be considered to be a functional dependent on $\rho$ the state operator. If considered in its functional form, a lower limit for $\tau(\rho)$ can be determined based on the Heisenberg time-energy uncertainty principle as is discussed in Beretta (2009a). The following shows that the $\tau$ for the various IQT operators such as those for internal dissipation, a heat interaction, and a mass interaction, can be put in a more simplified form than given by Beretta (2009a). An example of the IQT equation of motion in Massieu operator form that includes only internal dissipation is shown below.

$$\dot{\rho} = \left( \frac{1}{2\tau_D \sqrt{\langle \Delta M \Delta M \rangle}} \right) \{\Delta M, \rho\} \quad (4.85)$$

The Schrödinger term and other terms representing heat or mass interactions have been excluded. The quantity in braces on the right hand side of equation (4.85) represents the dissipation operator. The expression in parentheses represents the reciprocal of a scalar time functional

$$\frac{1}{\tau(\rho)} \geq \frac{1}{2\tau_D \sqrt{\langle \Delta M \Delta M \rangle}} \quad (4.86)$$

that has been derived by taking into consideration the lower limit imposed by the Heisenberg time-energy uncertainty relation,
\[ \Delta H \Delta t \geq \frac{\hbar}{2} \]  

(4.87)

From Beretta, (2010), parameter \( \tau_D \) is shown to be related to the Heisenberg limit by

\[ \langle \Delta H \Delta H \rangle \tau_D^2 \geq \frac{\hbar^2}{4} \]  

(4.88)

Solving for \( \tau_D \) results in

\[ \tau_D \geq \frac{\hbar}{2} \frac{1}{\sqrt{\langle \Delta H \Delta H \rangle}} \]  

(4.89)

Substituting this result into equation (4.86) leads to

\[ \tau \geq \frac{\Delta M \Delta M}{\langle \Delta H \Delta H \rangle} \sqrt{\langle \Delta M \Delta M \rangle} \]  

(4.90)

or

\[ \frac{1}{\tau} \leq \frac{1}{\hbar} \sqrt{\frac{\langle \Delta H \Delta H \rangle}{\langle \Delta M \Delta M \rangle}} \]  

(4.91)

For heat and mass interactions, \( \Delta M \) can be replaced by \( \Delta G \) or \( \Delta F \) where \( F \) and \( G \) are the Helmholtz and Massieu forms for these interactions. As a practical matter, it should be noted that the lower Heisenberg limit for the Beretta equation time functional is exceedingly small. Empirical data from experiments may require values for \( \tau \) that are orders of magnitude larger and that may well be nearly constant for the system involved.
Chapter 5 - Experimental Support for IQT

Since its development, there have been limited efforts to experimentally verify the IQT equation of motion

\[ \frac{d\rho}{dt} = -\frac{i}{\hbar}[H, \rho] - \frac{1}{\tau_D} D \]  

(5.1)

and, as a consequence, the theory of IQT. In an attempt at experimental verification, Çubukçu (1993) argues that unlike QM, IQT can predict the experimental results developed by Kukolich (1968) for the damped-oscillatory behavior seen in the absorption rate of transmitted light by rubidium atoms in the vapor phase in a magnetic field. However, to support this contention, he uses the analytical solution of the IQT equation of motion for a 2-level, spin-½ system given by Beretta (1985) even though the experimental rubidium spin system actually represents a 5-level spin system. Thus, the match between his solution and the actual experimental results is not perfect. Nonetheless, the implication is that the damping effects predicted by the IQT equation of motion are due to the irreversible relaxation of the spin states of the rubidium atom to stable equilibrium.

To improve on Çubukçu’s results, Kukolich’s experiment (Kukolich, 1968) is revisited herein along with some results from Nagel and Haworth (1966). The actual five-level system of Kukolich’s experiment is numerically (as opposed to analytically) modeled using the IQT equation of motion, equation (5.1). In addition, a new comparison is made with the experimental data of Turchette et al. (2000) for the relaxation of superposition states for a single ion in a Paul trap. The IQT equation of motion used is the one developed here, i.e., equation (4.13), which includes the RPHI operator. The following is based on results published by Smith and von Spakovsky (2011).

5.1 Comparisons of IQT Theory with Rubidium Spin Decay

5.1.1 Set-Up of the Rb Spin Experiment

Kukolich (1968) uses the spin states of rubidium to demonstrate the time dependence of the state operator of QM (i.e., the projector of the wave function). A diagram of the
The rubidium (Rb) atoms and a helium (He) buffer gas are contained in a closed glass vessel with an applied external magnetic field that is oriented along the z-axis. The technique of optical pumping with circularly polarized light is used to prepare the Rb atoms in the desired spin state. The He is used to slow the relaxation of the Rb due to collisions with other Rb atoms as well as collisions with the walls of the container.

Once the Rb atoms are in the uppermost spin energy eigenlevel, the direction of the magnetic field is changed suddenly to the x-direction, perpendicular to the z-axis. A photoelectric detector opposite the light source along the z-axis is used to measure the intensity of the light beam as a function of time. The intensity of the light that is transmitted through the Rb vapor is found to oscillate and can be used to determine the quantum eigenstates of the Rb atoms.

The spin states for Rb occur due to the coupling of the $\frac{3}{2}$ spin of the nucleus with the $\frac{1}{2}$ spin of the electrons. An energy level diagram is shown in Figure 5.2. The external magnetic field splits the energy eigenlevels $E_0$ and $E_1$ into sets of 5-level spin energy eigenlevels denoted as $F=1$ and $F=2$, respectively. The energies between each spin energy eigenlevel are multiples of Planck’s modified constant $\hbar$ as shown. The external circularly polarized laser light, which has a wavelength of 7948 Å, pumps the majority of the atoms into the highest energy eigenlevel (i.e., $F=2, \ |+2\rangle_z$), which leaves the Rb atoms in a spin-2 eigenstate.
The switching of the magnetic field to the $x$-direction changes the thermodynamic state of the Rb atoms. In QM, the new state or density operator (matrix) $\rho_{\text{new}}^{QM}$ as seen along the $z$-axis is calculated by means of the time-dependent von Neumann (or equivalent Schrödinger) equation or equivalently by the unitary (non-dissipative) transformation given by

$$\rho_{\text{new}}^{QM} = \left| \Psi^z \right|_{\text{new}} \left\langle \Psi^z \right|_{\text{old}} = U^{-1} \left| \Psi^z \right|_{\text{old}} \left\langle \Psi^z \right|_{\text{old}} U$$  \hspace{1cm} (5.2)

where $|\Psi^z\rangle_{\text{new}}$ (or its bra $\langle \Psi^z |_{\text{new}}$) is the new state vector and the unitary transformation matrix $U$ and its inverse $U^{-1}$ are Hermitian, i.e.,

$$U^{-1} = U^\dagger$$  \hspace{1cm} (5.3)

As done in Kukolich (1968), the unitary transformation matrix $U$ can be derived using the method outlined in Feynman, Leighton, and Sands (1965). The QM solution results in phases of state i.e., $\{J_z \omega_p / \hbar\}t = (-\varepsilon_i / \hbar)t$ for $i = -2, -1, 0, 1, 2$ that change periodically in time $t$. The precession frequency of the phase, $\omega_p$, is proportional to the absolute magnitude of the spin energy eigenvalues $\varepsilon_i$. As a consequence, the non-dissipative state operator $\rho_{\text{new}}^{QM}$ of the system must contain elements that oscillate with the precession frequency of the Rb atoms as well as twice this precession frequency, with the precession frequency being directly proportional to the strength of the applied magnetic field in the $x$-direction. After the transformation, the new state vector as seen from along the $z$-axis is expressed as
\[ |\Psi_{\text{new}}\rangle = \begin{bmatrix} \frac{1}{8} \cos 2\omega_p t + \frac{1}{4} \cos \omega_p t + \frac{3}{8} \\ \frac{1}{4} i \sin 2\omega_p t + \frac{1}{2} i \sin \omega_p t \\ \frac{1}{2} \sqrt{\frac{3}{8}} (\cos 2\omega_p t - 1) \\ \frac{1}{4} i \sin 2\omega_p t - \frac{1}{2} i \sin \omega_p t \\ \frac{1}{8} \cos 2\omega_p t - \frac{1}{2} \cos \omega_p t + \frac{3}{8} \end{bmatrix} \]  

(5.4)

where the transformed state vector \( |\Psi_{\text{new}}\rangle \) (or state operator \( \rho_{\text{new}}^{\text{QM}} \)) is that for a pure state (i.e., a thermodynamic state with zero entropy).

After the field direction is switched, the transmitted light from the same light source that is used for the optical pumping is employed to produce a signal whereby the thermodynamic state of the system can be determined. This is deduced from the intensity of the light transmitted through the cell containing the Rb atoms given by (Kukolich, 1968)

\[ I = I_0 - A = I_0 - \frac{3}{2} C + 2C \cos \omega_p t + \frac{3}{2} C \cos 2\omega_p t \]  

(5.5)

where \( I_0 \) is the intensity of the light source and \( A \) the magnitude of the light absorbed by the atoms expressed as

\[ A = \frac{7}{2} C - 2C \cos \omega_p t - \frac{3}{2} C \cos 2\omega_p t \]  

(5.6)

As seen in equation (5.4), the intensity contains two precession frequencies: \( \omega_p \) and \( 2\omega_p \).

A diagram of \( I \) as a function of time is shown in Figure 5.3 and clearly shows the oscillatory behavior of the thermodynamic state of the Rb atoms also seen in the experimental results given in Figure 5.4. As expected, the damping seen in the experimental results does not appear in Figure 5.3 since the unitary transformation of QM is reversible and damping is an inherently irreversible phenomenon. The damping, in fact, indicates that there is a relaxation from the initial non-equilibrium state in which the Rb atoms are placed to one of stable equilibrium. In addition, as noted in Kukolich (1968), the relative amplitude between the two frequency components in Figure 5.4 differ from the expected theoretical value in part because the photocell attenuates the fundamental frequency more than the double frequency component.

Finally, the braces under some of the oscillations in part (a) of Figure 5.4 indicate a “stair step” aspect of the data not attributable to a simple exponential decay of the signal. As will be seen below, both this aspect and the damping are captured by the IQT simulation.
Figure 5.3. Time-dependent photocell current as calculated for a spin-2 system without dissipation (Kukolich, 1968). Reprinted with permission, American Institute of Physics, copyright 1968.

Figure 5.4. Experimental trace of the photocell current for two precession frequencies ((a) $\omega_p$ and (b) $2\omega_p$) after the field is switched to the $x$-direction (Kukolich, 1968). Reprinted with permission, American Institute of Physics, copyright 1968.

In an experiment similar to that of Kukolich (1968), Nagel and Haworth (1966) use the magnetic field of the earth, which is oriented in the $x$-direction, instead of an applied external field to produce the oscillations. Their results shown in Figure 5.5 indicate an initial spin attenuation that is more gently curved than would be indicated by a simple exponential decay. In fact, these relaxation curves look more like the gradual, S-shaped curves that are predicted by IQT. The IQT equation of motion, equation (5.1), characteristically behaves such that sparsely occupied energy eigenlevels for a system gradually increase their occupation probabilities at the expense of those with larger initial occupation probabilities. Clearly, the same gradual, S-shaped drop off is not seen in the Kukolich experiment. Although one can only speculate as to why, since Kukolich makes no comment, it is reasonable to assume that only the latter part of the signal, which corresponds to the Nagel-Haworth experiment, is reported in Kukolich.
5.1.2 Predictions of the IQT Formulation for Rb Relaxation

To initiate the solution of the IQT equation of motion for the Rb relaxation, a density operator, which is a slight perturbation of the density or state operator $\rho$, that represents the thermodynamic state of the system after the magnetic field is switched to the x-direction, is chosen. Thus, the initial state operator $\rho_{initial}$ is taken as some small perturbation of $\rho_{new}^{QM}$ in equation (5.2) evaluated at $t = 0$. The IQT solution assumes that each Rb atom can be treated as a separate, isolated system. This assumption is valid at sufficiently low pressures as suggested by Çubukçu (1993) based on Franzen’s (1959) measurements of relaxation time as a function of Rb vapor pressure. The Franzen (1959) data indicate that the time to relax increases with decreasing pressure until the pressure is sufficiently low after which it plateaus out to a nonzero value, implying that the relaxation remains even in the absence of collisions, i.e., when as collisions as the driving mechanism for relaxation become negligible. Thus, the gradual relaxation to stable equilibrium is attributed to each atom’s own internal relaxation from a state of non-equilibrium to one of stable equilibrium and not due to collisions with other atoms; (i.e., Rb, atoms buffer gas atoms or with the wall).

To model this relaxation, the system of equations which result from equation (5.1) for this 5-level, spin-2 system is written as
\[
\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar} [H, \rho]_{ij} - \frac{1}{\tau_D} D_{ij}
\]  
(5.7)

where the \( \rho_{ij} \) are the elements of the density matrix (state operator) that are found as functions of time and \( i \) and \( j \) each vary from 1 to 5. The first term on the right hand side of Eq. (5.7) are the commutator elements that represent the periodic behavior of the relative phases between the spin energy eigenlevels of each Rb atom. The second term is the elements of the dissipation operator of IQT expressed as

\[
D_{ij} = \begin{bmatrix}
\rho_{ij} (\ln \rho)_{ij} & \rho_{ij} & E_{ij} \rho_{ij} \\
\sum \rho_{ii} (\ln \rho)_{ii} & 1 & \sum E_{ii} \rho_{ii} \\
\sum E_{ii} \rho_{ii} (\ln \rho)_{ii} & \sum E_{ii} \rho_{ii} & \sum E_{ii}^2 \rho_{ii}
\end{bmatrix}
\]  
(5.8)

Because the state involves the decay of the relative phases between the spin energy eigenlevels of each Rb atom, the operators \( H \) and \( \rho \) do not commute so both diagonal and off-diagonal elements of \( \rho \) are included in the solution, and, of course, \( (\ln \rho)_{ij} \) denotes the matrix elements of the natural logarithm of the density operator\(^{10}\).

The results from the IQT equation of motion are seen in Figure 5.6, which shows the evolution of the density operator for the 5-level, spin-2 Rb system with internal dissipation. The upper blue traces result from the diagonal terms of the state operator (the energy occupation probabilities), while the traces in red and green represent evolutions due to the off-diagonal terms. The time constant \( \tau \) is chosen to qualitatively match the rate of dissipation shown in the Kukolich data. The solution is used in Eq. (5.5) to calculate the amount of transmitted laser light.

A close-up view of the IQT solution is seen in Figure 5.7 where it is evident that the two different frequencies contained in the waveform play a role in the time evolution of the state operator. In other similar experiments described in Balabas et al. (2010) and Happer, Jau, and Walker (2010), the light frequency unlike in the Kukolich experiment is detuned far from

---

\(^{10}\) Operator \( \ln \rho \) is the operator with the same eigenvectors as \( \rho \) and eigenvalues \( \ln \rho \) where the \( \rho_k \) are the eigenvalues of \( \rho \). Therefore, \( (\ln \rho)_{ij} = \sum_k u_{ik} (\ln \rho_k) u_{ki} \), where \( u_{ik} \) is the unitary matrix having as columns the eigenvectors of \( \rho \).
Figure 5.6. Evolution as predicted by IQT of the density matrix for the 5-level, spin-2 Rb system.

Figure 5.7. A detailed view of the IQT result for the density matrix evolution of the 5-level, spin-2 Rb system.

resonance so as to reduce any disturbance by the probe beam. As a result, the double frequency component is suppressed and the signal is dominated by just the precession frequency.

Since the relaxation to stable equilibrium is due to dissipation (i.e., the destruction of exergy, which is modeled by the second term on the right hand side of the IQT equation of
motion (equation (5.7)), the entropy changes and evolves as shown in Figure 5.8. As is evident from this figure, the entropy evolves somewhat slowly initially and then quickly increases until in the final stage it shows an exponential-like approach to its maximum or stable equilibrium value.

![Figure 5.8](image)

**Figure 5.8.** The IQT result for the entropy as a function of time for a 5-level, spin-2 Rb system.

Finally, in an analogous fashion to equation (5.5) in Kukolich (1968), the state operator \( \rho \) is used to calculate the amount of transmitted light. The relative probabilities of photon absorption for the four lowest energies are given in Kukolich (1968) as derived from Messiah (1962, 1976). Only the four lowest spin energies are able to absorb photons since there are no transitions that above the \(|+2\rangle\) energy state. These absorption probabilities are multiplied by the respective lowest four diagonal elements of \( \rho \) which are then summed together to represent the IQT version of the absorption function \( A \) of equation (5.6). The result for the transmitted light is presented in Figure 5.9 and follows the same trends as the experimental data of Kukolich and Nagel and Haworth presented in Figures 5.4 and 5.5. The initial period of relaxation starts out relatively gradually, much like the result seen in Figure 5.5, an effect which is commonly seen in IQT simulations. The reason for this is that it takes some time for energy sharing between the occupied and unoccupied energy eigenlevels of the system to grow. For the 5-level, spin-2 Rb system, the lower four system eigenlevels start out with very low occupation probabilities due to
the optical pumping of the Rb atom into the fifth and highest level. The IQT simulation predicts a lag before the internal energy begins to be extensively shared with the lower four spin levels.

A close up view of the predicted QT transmission curve is shown in Figure 5.10 and shows overall good agreement with the Kukolich data. Notably, the IQT simulation is able to capture the uneven stair-step feature of the wave minima, which contrasts with the smooth envelope produced by the decaying exponentials typically used in QM as is shown in Figure 5.11. The double frequency component is seen to damp out more rapidly than for the Kukolich
Figure 5.11. The transmission amplitude as calculated by QM and multiplied by a decaying exponential function with the extrema of the curve following the exponential envelope.

The likely reason is that the simulation leaves out the selective damping effects of the primary frequency of the signal by the optical filters and photocell that occurred in the experiment.

5.2 Trapped Ions: The Turchette et al. Experiment

5.2.1 Experimental Set-up

In the experiment of Turchette et al. (2000), a thermodynamic system consisting of a single trapped Be\(^+\) ion contained in a Paul trap is put into various quantum superposition states much like in the “particle in a box” models that are used in physics texts. The decay of the initial state is observed and measured after the ion trap is put into contact with a range of engineered external heat sources. A schematic of the Paul trap is shown in Figure 5.12.

The edges of the slots serve as electrodes through which the RF (radio frequency) fields are produced to trap the ion as well as to input the noise signals used to serve as an external heat source. The strength of the fields is quadratic, so the particle behaves as a quantum harmonic oscillator within the trap. The harmonic superposition or “cat” or “motional” states that are produced in the experiments are also known as Fock states, and density matrices describing these states contain only diagonal elements (Turchette et al., 2000).
The measurement of the amount of decoherence (i.e., in the view of IQT, the amount of dissipation) over the time interval is done through interferometry techniques. Nuclear spin states (up and down) are excited in the Be\(^+\) ion and combined by means of optical pumping and laser cooling methods with the superpositions of the motional eigenstates of interest. The spins constitute a “carrier” signal that enables the degree of decoherence of the cat states to be readily measured. The resulting quantum (thermodynamic) state after preparation can be written in terms of the state vector such that

\[
|\psi\rangle = \frac{1}{\sqrt{2}} (|\downarrow\rangle|\alpha\rangle + |\uparrow\rangle|\alpha\rangle)
\]

where the arrows signify spin up or spin down and \(\alpha\) is the particular cat state superposition between the ground state \(|0\rangle\) and some higher energy oscillator state \(|n\rangle\). Because the spin states are correlated with the energy eigenstates of the harmonic oscillator, any changes or degradation of the cat state will result in proportional changes between the phases of the up and down (|\uparrow\rangle and |\downarrow\rangle) eigenstates.

During the experimental procedure, a state as shown in equation (5.9) is created and immediately coupled to a heat bath. After a given delay, typically 3\(\mu\)s, a measurement is made. The phase shift between the spin components is seen as a loss of signal contrast from which the
magnitude of decoherence of the cat state can be calculated. The heat bath consists of a noise spectrum of a given mean frequency and power that is applied to the fields containing the ion in the Paul trap. The mean frequency of the noise corresponds to the temperature of the heat bath while the power (in volts$^2$) corresponds to the strength of the heat source coupling to the system. Numerous measurements are conducted to produce ensemble average values that make up each experimental data point. The time intervals between the application of the heat source and when the measurements are taken are held constant. The variation of the power turns out to give results that are close to being the same as keeping the strength of the heat source constant and varying the measurement time intervals and is evidently easier to do experimentally.

5.2.2 Comparison of IQT Predictions with the Trapped Ion Data

IQT simulations are compared with the relaxation data for the ion and instead of equation (5.1) use equation (4.13) of Chapter 4, which includes the RPHI operator to account for the heat interaction that occurs between the heat source and the system. The simulations use 100 equally spaced energy eigenlevels to represent the lowest eigenlevels of the trap. The superposition eigenstates that are studied are the $|1\rangle$, $|2\rangle$ and $|3\rangle$ cat states from Turchette et al. (2000) where $|1\rangle$ is the state associated with the energy eigenlevel one level above the ground energy level, $|2\rangle$ two levels above, and $|3\rangle$ three levels above. In the experiments, the power applied to the heat source $\langle V^2 \rangle$ is used to represent the relaxation time.

The initial state and relaxation time constants are varied to fit the IQT simulation results with the experimental probability distribution versus time data of Turchette et al. (2000) as well as with the energy versus entropy plots created using the experimental data of Turchette et al. (2000). The temperatures of the heat reservoirs of the experiment are estimated by noting the tightness of the probability distribution for the data as stable equilibrium is approached. Determining the initial state of the system for the IQT simulations is somewhat problematic since it is not specified in Turchette et al. (2000) but is again estimated with reasonable success based on the experimental data.

Comparisons between the IQT results and the experimental data for the lowest 5 energy eigenlevels of the cat state are shown in Figures 5.13 to 5.15. The experimental data is indicated by the symbols. The solid lines in part a) of these figures are the theoretical probabilities
predicted from the QSM master equation used in Turchette et al. (2000). The solid lines in part b) are the probabilities predicted by IQT using equation (4.13), the internal dissipation operator together with the rotated heat interaction (RPHI) operator. The time constants used for the IQT

![Image](image1.png)

**Figure 5.13.** Comparison of the experimentally measured dissipative decay of cat state $|1\rangle$ for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. (2000) using a QT master equation and with b) that predicted by the IQT equation of motion that includes the RPHI operator term. Figure a) reprinted with permission from: Turchette, Q.A., Myatt, C.J., King, B.E., Sackett, C.A., Kielpinski, D., Itano W.M., Monroe, C. and Wineland, D.J. (2000). Decoherence and Decay of Motional Quantum States of a Trapped Atom Coupled to Engineered Reservoirs, *Phys Rev A*, 62, 053807. Copyright 2000 by the American Physical Society.

Simulation in Figure 5.13 are $\tau_D=20.0$ and $\tau_Q=27.0$ for the dissipation and heat interaction terms, respectively. In Figures 5.14 and 5.15, $\tau_D$ is still 20 but $\tau_Q$ changes to 20.0 and 25.0, respectively. The scaled reservoir temperature in each figure for a Boltzmann constant set to 1.0 is estimated to be 0.055, 0.11, and 0.15, respectively.
Although both the QT and IQT simulations fit the data well, QT views the “dissipation” predicted by its master equation as a loss of coherence, resulting from the loss of correlations (information) between the system and the heat reservoir, which cyclically buildup and then are lost (i.e., dissipate) as the system relaxes to stable equilibrium. Such a loss is not physical since it is due solely to the exogenous statistics, i.e., to a loss of information about the state of the

![Graph a)

Figure 5.14. Comparison of the experimentally measured dissipative decay of cat state $|2\rangle$ from Turchette et al. (2000) for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. (2000) using a QT master equation and with b) that predicted by the IQT equation of motion that includes the RPHI operator term. Figure a) reprinted with permission from the American Physical Society, copyright 2000.

In contrast, IQT views the “dissipation” as the internal destruction of exergy, i.e., available energy (Gyftopoulos and Beretta, 2005) resulting from a spontaneous redistribution of energy among the available eigenlevels. Thus, the “dissipation” is due to the endogenous measurement statistics of QM alone and is, therefore, physical.
5.2.3 IQT Predictions in $\langle E \rangle - \langle S \rangle$ Space Compared with Experiment

As shown in the previous sections, the IQT trajectories match the Turchette et al. (2000) experimental relaxation data well. The results for these QT simulations are also plotted on the energy $\langle E \rangle$ versus entropy $\langle S \rangle$ diagrams shown in Figures 5.17 to 5.19. For the 5 lowest eigen-

![Figure 5.15](image1.png)

**Figure 5.15.** Comparison of the experimentally measured dissipative decay of cat state $|3\rangle$ from Turchette et al. (2000) for the lowest 5 energy eigenlevels with a) that predicted by Turchette et al. (2000) using a QT master equation and with b) that predicted by the IQT equation of motion that includes the RPHI operator term. Figure a) reprinted with permission from the American Physical Society, copyright 2000.

levels, the experimental data is given in dark blue, the values predicted by the QT master equation are in light blue, and the curve predicted from QT is in magenta. Note that the fact that the experimental data as well as the QT and IQT trajectories curve back on themselves is, of course, physically impossible, i.e., violates that Second Law. However, this occurs here solely due to the fact that these trajectories are only based on the lowest 5 energy eigenlevels. When all 100 eigenlevels are considered, the result is the red curves, which show the evolution of the 100 energy eigenlevel model as predicted by IQT from the initial state designated by the cross in
magenta to a state of mutual stable equilibrium with the heat reservoir. Clearly, for all three cat state relaxations, the IQT simulations do a good job of matching the experimental data.

The curves in Figures 5.16 to 5.18, whether they are from the experimental data, from QT or IQT are seen to support the idea of an irreversible relaxation to stale equilibrium. In all cases, the initial paths of the trajectories are not directly toward the reservoir point on the system equilibrium curve. The trajectories must, therefore, bend and take a curved path on their way to mutual stable equilibrium with the reservoir. In addition to the attractive effect of the reservoir, an additional effect causes the state to move in a horizontal direction, an effect IQT calls internal dissipation. The theory of IQT claims that the second effect is spontaneous. According to IQT,

![Diagram](image)

**Figure 5.16.** Non-equilibrium evolutions in thermodynamic state of cat state $|1\rangle$ on an energy versus entropy diagram when only considering the lowest 5 energy eigenlevels and in the case of the IQT simulation 100 eigenlevels as well.

the magnitude of the internal dissipation is not affected by the strength of the reservoir. As discussed in Chapter 4, the amount of curvature should vary with changes in the strength of the heat source, something that should be testable using the experimental apparatus of Turchette et al. (2000). Indeed Rb spin systems and trapped ions look like they would provide other possibilities for directly testing the IQT theory as well.
Figure 5.17. Non-equilibrium evolutions in thermodynamic state of cat state $|2\rangle$ on an energy versus entropy diagram when only considering the lowest 5 energy eigenlevels and in the case of the IQT simulation 100 eigenlevels as well.

Figure 5.18. Non-equilibrium evolutions in thermodynamic state of cat state $|3\rangle$ on an energy versus entropy diagram when only considering the lowest 5 energy eigenlevels and in the case of the IQT simulation 100 eigenlevels as well.

5.3 Concluding Remarks

Simulations using the equation of motion of IQT are seen to correspond closely to data from two experiments that show non-equilibrium relaxations at atomistic scales. Thus, there
appears to be support for the idea as proposed by IQT that dissipation due to internal irreversibilities occur for systems even at these small scales, i.e., that there is no “irreversibility paradox”. The findings though not conclusive nonetheless warrant the development of additional experiments specifically designed to verify the claims of IQT that the entropy is indeed a fundamental property of matter in the same way that inertial mass, energy, and momentum are. Possible experiments towards this end are discussed in the Conclusions section in Chapter 8.
Chapter 6 - IQT Models for Simulating the Non-Equilibrium Behavior of Hydrogen Storage on a Carbon Nanotube

This chapter describes the work and extensions thereof reported in previous papers (Smith et al., 2010; Smith, Verda and von Spakovsky, 2008; von Spakovsky, Smith, and Verda, 2008; Smith and von Spakovsky, 2007) of using IQT to model the non-equilibrium evolution in state of hydrogen storage on and in a carbon nanotube. The thermodynamic system of interest is the hydrogen, which is assumed isolated and contained within the walls of a 250 nm$^3$ tank at the center of which lies the carbon nanotube. The system boundaries coincide with the walls of the tank. To model the evolution in state of the system, the energy eigenvalues and eigenfunctions for the system are first obtained and then the occupation probabilities associated with each energy level as a function of time are determined.

The original contributions presented include not only the idea of using IQT to model a nanoscale problem such as hydrogen storage on a carbon nanotube but also the addressing of several significant technical challenges in the implementation of the model. As outlined in Chapter 1, among these is the development of an elementary but accurate quantum mechanical model for the movement of hydrogen molecules near the specified single-walled carbon nanotube. The model accounts for both external (translation) and internal (rotation) degrees of freedom as well as for the interactions between hydrogen molecules and the hydrogen molecules and the carbon atoms. The solution for the translational two-body energy eigenvalue problems uses a finite element approach utilizing an unstructured finite element grid. Also discussed is the scheme that is used to combine the solutions of the two-body problems so as to create energy eigenlevels for a system of multiple particles. The model also requires the development of a methodology for accurately approximating an extremely large number of energy eigenlevels with a much smaller representative set of energy eigenlevels. Finally, the implementation of the IQT
equation of motion and its time-varied solution for this system using an initial state far from equilibrium is presented.

For our application, the energy eigenvalue problem, which is a many-body problem that for dilute and moderately dense gases can be modeled using virial expansion theory (Tien and Lienhard, 1979; Hill, 1956), is first solved in 3D to determine the so-called primitive-level energy eigenvalues and eigenstates of the system. This information is then used in a combinatorial problem to determine the system-level energy eigenvalues and eigenstates. The system eigenenergies are subsequently used in the nonlinear IQT equation of motion, equation where the density operator $\rho$ is diagonal, (Beretta, 1981, 1984, 2005, 2006a,b, 2007, 2008a; Beretta et al., 1984, 1985; Gheorghiu-Svirschevski, 2001) to determine the evolution (relaxation) of the thermodynamic state of the system to stable equilibrium, starting from some initially prepared state far from stable equilibrium. The diagonal version of the $\rho$ operator is used because it captures the dynamics of interest and is less computationally prohibitive (of order $O(n)$ vs. $O(n^2)$) given the large number $n$ of the energy eigenvalues in the model. The results from techniques such as MD, which treat the molecules as classical particles, strongly suggests that the quantum interference effects provided by the off-diagonal terms are in most cases negligible.

The spatial distribution of the hydrogen molecules as a function of time is determined using linear combinations of the system eigenfunctions as weighted by the evolving probabilities of the state of the system. The results of the simulations provide a quantification of the entropy generated due to irreversibilities at an atomistic level. The results show in detail the trajectory of the state of the system as the hydrogen molecules, which are initially spread out in the tank, eventually become more concentrated near the carbon atoms of the nanotube.

### 6.1 System Description

The thermodynamic system under consideration is that of 4 H$_2$ molecules contained in a 5 nm x 5 nm x 10 nm tank with a carbon nanotube at its center. The nanotube is constructed based on Frey and Doren (2005) and is a (15, 15) armchair carbon nanotube. The tube consists of a total of 900 atoms. The radius and the length of the tube are 1.017 nm and 3.56 nm, respectively. The carbon nanotube depicted in Figure 6.1 is located at the center of the tank so that the center of the tube is placed at coordinates (5.0, 2.5, 2.5). The red spheres represent the carbon atoms.
The bonds connecting these atoms are not represented. To simplify the model, it is assumed that the atoms and the structure of the nanotube remain stationary and do not vibrate.

**6.2 Governing equations**

Two systems of equations govern the evolution in time of the thermodynamic state and position of the H\(_2\) molecules in the tank: one based on the IQT equation of motion and the other on the energy eigenvalue problem. The former equation for this single constituent, isolated system is expressed in operator format by

\[
\frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] - \frac{1}{\tau} D
\]  

while the latter is written as

\[
Hu_i(x_1, x_2, ..., x_n) = E_iu_i(x_1, x_2, ..., x_n)
\]

for \(i = 1, 2, ..., L\). In equation (6.1), \(H\) is the Hamiltonian operator, \(\tau\) a scalar time constant or functional, and \(-D/\tau\) a dissipation term referred to herein as the dissipation operator. The dissipation operator is a function of the state operator \(\rho\), \(ln\rho\), and \(H\) the Hamiltonian and captures the nonlinear dynamics of an irreversible process by pulling \(\rho\) in the direction of steepest entropy increase while maintaining constant energy for the system.

As to the system of equations (6.2), \(E_i\) and \(u_i\) are the system-level energy eigenvalues and eigenfunctions, the \(\bar{x}_k\) are the 3D particle position vectors, and \(L\) is the number of system-level energy eigenvalues. For the energies considered in this paper, only translational and rotational modes of energy storage and their degeneracies are relevant and, thus, included in the quantum mechanical description. These modes of storage are modelled and solved separately here. The translational as a set of two-body problems is solved numerically using a finite element approach and the rotational is solved analytically. For translational modes, the Hamiltonian operator is given by

\[
H = \sum_{k=1}^{n} \left( -\frac{\hbar^2}{2m} \nabla^2_k + V_k(x_1, x_2, ..., x_n) \right)
\]

and represents the kinetic and potential energies of the translational motions of the H\(_2\) particles in the tank and the intermolecular interactions between H\(_2\) particles and between the H\(_2\) and the C particles of the carbon nanotube.
6.2.1 The Energy Eigenvalue Problem for Rotation

Analytically, the rotational mode of energy storage for each H$_2$ molecule is modelled in its simplest form by assuming a rigid rotor model. The resulting eigenfunctions for the two degrees of rotational freedom are a product of an azimuthal quantum number ($m$) dependent exponential (Hatsopoulos and Gyftopoulos 1979) and an angular momentum quantum number ($l$) dependent Legendre polynomial $P_l^m$ (Knuth, 1966) such that (Tien and Lienhard, 1979)

$$u_{l,m}(\theta, \phi) = \frac{1}{2\sqrt{l!}} P_l^m(\cos \theta) e^{i m \phi}$$

(6.4)

The corresponding rotational energy eigenvalue is expressed as (Tien and Lienhard, 1979)

$$\varepsilon_l = \frac{\hbar^2}{2I} l(l + 1) \quad l \geq |m|, \quad m = 0, \pm 1, \pm 2, \ldots$$

(6.5)

where $I$ is the moment of inertia equal to $m_{rm} r^2$, $r$ the distance separating the hydrogen nuclei, and $m_{rm}$ the reduced mass defined as

$$m_{rm} = \frac{m_1 m_2}{m_1 + m_2} = \frac{m_R}{2}.$$ 

(6.6)

To account for the degeneracies of the number of rotational orientations as well as of the spin that leads to ortho- and para-hydrogen, the following expressions are used for the rotational and the ground state spin degeneracies (Tien and Lienhard, 1979):

---

**Figure 6.1.** Depiction of the carbon nanotube used for the simulations of hydrogen storage.
where \( g_0 \) is the ground-state spin degeneracy of a single nuclei equal to \( 2n+1 \) and \( n \) is the quantum spin number, which for the ground state is \( \frac{1}{2} \). Equation (6.8) represents the symmetric spin degeneracy which leads to ortho-hydrogen and equation (6.9) the anti-symmetric spin degeneracy which results in para-hydrogen.

### 6.2.2. The Energy Eigenvalue Problem for Translation for Multiple Particles

The computational difficulties of the eigenvalue problem, which represents a multi-body problem, quickly augment as the number of particles in the system increases. In fact, it may even become impossible to solve. To circumvent this, a set of 2-body problems (Hatsopoulos and Gyftopoulos 1979), which define the motions and interactions between nearest neighbor pairs of \( \text{H}_2 \) molecules and between each of the \( \text{H}_2 \) molecules and the C atoms of the nanotube, are assumed. Such an approach has been used very successfully when using IQT to derive stable equilibrium property relations such as, for example, the virial equation of state.

For the \( \text{H}_2 \)-C motions and interactions, which are of interest here, the 2-body problem is written as

\[
H_k u_j(\vec{x}_k) = \epsilon_{kj} u_j(\vec{x}_k), \quad j = 1, 2, ..., M
\]

for \( k = 1, 2 \) (i.e., the 1\textsuperscript{st} and 2\textsuperscript{nd} \( \text{H}_2 \)) and the translational Hamiltonian operator is given by

\[
H_k = \frac{-\hbar^2}{2m} \nabla_k^2 + \sum_l V_l(\vec{x}_k)
\]

where the summation includes all of the \( \text{H}_2 \)-C interactions. The potential functions \( V_l(\vec{x}_k) \) are expressed by 6-12 Lennard-Jones potentials, i.e.,

\[
V(\vec{x}_k) = 4\mu \left[ \left( \frac{\sigma}{r(\vec{x}_k)} \right)^12 - \left( \frac{\sigma}{r(\vec{x}_k)} \right)^6 \right]
\]

where \( r \) is the distance between molecules/atoms. Values for the fitting parameters \( \mu \) and \( \sigma \) specific to a particular interaction are given in Table 1.
Table 6.1 Fitting parameters for the L-J potential.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>(\mu(l))</th>
<th>(\sigma(\text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)-H(_2)</td>
<td>5.24 \times 10^{-22}</td>
<td>0.2915</td>
</tr>
<tr>
<td>H(_2)-C</td>
<td>4.502 \times 10^{-22}</td>
<td>0.3137</td>
</tr>
</tbody>
</table>

In equation (6.10), each \(\varepsilon_{kj}\) is a paired particle or so-called primitive-level energy eigenvalue related to the system-level energy eigenvalues \(E_{ki}\) by

\[
E_{ki} = \sum_{j=1}^{M} V_{ij} \varepsilon_{kj}
\]

where \(M\) is the total number of primitive energy eigenlevels utilized and \(V_{ij}\) (the so-called occupation number (Hatsopoulos and Gyftopoulos 1979)) is the number of paired H\(_2\)-H\(_2\) molecules for a given primitive energy eigenlevel \(j\) that occupies a given system energy eigenlevel \(i\). If only a single pair of H\(_2\) molecules were present in the tank (i.e., for \(N=1\)), all the occupation numbers would be one. For the case of a closed, non-reacting system and \(N \geq 2\), the number of system energy eigenlevels \(L\) is given by

\[
L = (N + M - 1)! / (N!(M - 1)!) \quad (6.14)
\]

In general, the number of primitive energy eigenlevels is infinite for the translational Hamiltonian operator since this operator is unbounded. However, because of the computational burden of an infinite number of levels, a finite number \(P\) is assumed and of this finite number only a subset \(M\) is actually used, an assumption which under certain conditions is justified as described below.

For the paired H\(_2\)-H\(_2\) motions, the 2-body problem is written as

\[
H_{1,2} u_j (\vec{x}_1, \vec{x}_2) = \varepsilon_{1,2} u_j (\vec{x}_1, \vec{x}_2), \quad j=1, \ldots, M \quad (6.15)
\]

and the Hamiltonian as

\[
H_{1,2} = \sum_{k=1}^{2} -\frac{\hbar^2}{2m} \nabla_k^2 + V(\vec{x}_1, \vec{x}_2) \quad (6.16)
\]

This problem can equivalently be decomposed into a reduced mass \((rm)\) and a center of mass \((cm)\) problem (Shankar, 1994) such that

\[
H_k u_j (\vec{x}_k) = \varepsilon_{kj} u_j (\vec{x}_k), \quad j=1,2, \ldots, M \quad (6.17)
\]
In equation (6.17), \( k = rm, cm \); and the Hamiltonian for both the reduced mass and center of mass problems is expressed by

\[
H_k = \frac{-\hbar^2}{2m_k} \nabla_k^2 + V(\bar{x}_k)
\]

(6.18)

For the reduced mass problem, the potential function \( V(\bar{x}_k) \) is given by the 6-12 Lennard-Jones potential (equation (6.12)), while for the center of mass, it is zero. Furthermore, the reduced mass is defined by equation (6.6) above, the center of mass by

\[
m_{cm} = m_1 + m_2
\]

(6.19)

and the coordinates for each problem by

\[
\bar{x}_{rm} = \bar{x}_2 - \bar{x}_1
\]

(6.20)

\[
\bar{x}_{cm} = \frac{m_1 \bar{x}_1 + m_2 \bar{x}_2}{m_1 + m_2}
\]

(6.21)

Since the center of mass contribution in this case is found to be smaller by two orders of magnitude relative to that of the reduced mass, it is neglected from here on.

Once the solutions to the set of 2-body problems listed above have been determined, they are assembled into a set of primitive-level energy eigenfunctions given by

\[
u_p(\bar{x}) = u_{ijk}(\bar{x}_1, \bar{x}_2, \bar{x}_{rm}) = u_i(\bar{x}_1)u_j(\bar{x}_2)u_k(\bar{x}_{rm}) \quad i, j, k = 1, \ldots, M \quad p = 1, \ldots, M^3
\]

(6.22a)

\[
u_p(\bar{x}) = u_{C-H_2(i)}^{(1)}(\bar{x}_1)u_{C-H_2(j)}^{(2)}(\bar{x}_2)u_{H_2-H_2(k)}(\bar{x}_{rm}) \quad i, j, k = 1, \ldots, M \quad p = 1, \ldots, M^3
\]

(6.22b)

\( M \) represents the number of energy eigenvalue problems solved for each two-body problem. Note that the energy eigenfunctions for rotation are not included in equation (6.22) because the spatial and not the localized effect of rotational orientation for each hydrogen molecule in the tank is of interest here. However, as seen in equation (6.23), the rotational energies are included in the overall primitive-level energy eigenvalues since they are indeed significant, i.e.,

\[
\varepsilon_p = \varepsilon_{ijkl} = \varepsilon_{1i} + \varepsilon_{2j} + \varepsilon_{rmk} + \varepsilon_{rot} \quad i, j, k = 1, \ldots, M \quad l = 1, \ldots, R_c \quad p = 1, \ldots, \mathcal{P}
\]

(6.23a)

\[
\varepsilon_p = \varepsilon_{C-H_2(i)}^{(1)} + \varepsilon_{C-H_2(j)}^{(2)} + \varepsilon_{H_2-H_2(k)} + \varepsilon_{rot} \quad i, j, k = 1, \ldots, M \quad l = 1, \ldots, R_c \quad p = 1, \ldots, \mathcal{P}
\]

(6.23b)

\( \mathcal{R_c} \) and \( \mathcal{P} \) are the total number of possible degenerate rotational and primitive-level energy eigenvalues, respectively that could be utilized. As explained below, the set of \( \mathcal{P} \) primitive levels represents a much larger set than the set of \( M \) primitive levels actually utilized.
Now, when two or more \(H_2-H_2\) pairs are present (i.e., when \(N \geq 2\)), a set of system-level energy eigenfunctions and eigenvalues must be determined based on the primitive-level ones utilized (i.e., the set of \(M\) levels). This is done by first determining the \(\nu_{ip}\) coefficients in equation (6.24) via a combinatorial problem which fills an \(L \times M\) matrix of possible occupation energies from which the system-level energy eigenvalues, \(E_i\), are found using

\[
E_i = \sum_{p=1}^{M} \nu_{ip} E_p
\]  

(6.24)

To find the system-level \(u_i\), the primitive-level \(u_p\) are first projected from the decomposed space represented by \((\tilde{x}_1, \tilde{x}_2, \tilde{x}_m)\) back onto 3D space represented by \((\tilde{x} = \{x, y, z\})\) and then combined using

\[
u_{ip} = \prod_{p=1}^{M} \left( u_p(\tilde{x}) \right)
\]  

(6.25)

This last result, equation (6.25), is a set of spatially dependent eigenfunctions, which are independent of time since the Hamiltonian operator and the boundary conditions (i.e., the tank walls and location of the carbon atoms) are fixed.

### 6.2.3 The Equation of Motion

To complete the thermodynamic description of the process, which the system of Figure 6.1 undergoes, the solutions of the energy eigenvalue problem just described must be combined with those of the system of equations formed by the equation of motion, equation (6.1). In addition, since this is an initial-value problem, an initial condition for the system, i.e., an initial non-equilibrium state represented by an initial state operator or density matrix \(\rho\) must be determined. This can be done randomly or by using the procedure outlined in Beretta (2006a,b) and in Smith and von Spakovsky, (2007), which finds a set of partially canonical equilibrium states and then perturbs them to find a set of initial non-equilibrium states.

Assuming that \(\rho\) is diagonal in the \(H\) representation, \(H\) and \(\rho\) commute and equation (6.1) reduces to

\[
\frac{d\rho}{dt} = -\frac{1}{\tau} D
\]  

(6.26)

which is equivalent to equation (3.123). Note that according to the Beretta equation, an initial \(\rho\), which is diagonal in the \(H\) representation, remains so at all times \(t\). This special class of
diagonal initial states is used here for simplicity and because in this case the eigenvalue \( \rho_i \) of \( \rho \) is readily interpreted as the probability of finding the system in the system-level energy eigenvalue \( E_i \). Nonetheless, it should be emphasized that the IQT equation of motion yields well-defined evolutions for arbitrary non-equilibrium initial states \( \rho \) not necessarily diagonal in the \( H \) representation, i.e., when \( H \) and \( \rho \) do not commute.

Equation (6.26) written out in terms of the eigenvalues \( \rho_i \) (for this particular case, the diagonal elements of \( \rho \)) yields (for \( i = 1, \ldots, L \))

\[
\frac{d\rho_i}{dt} = \frac{1}{\tau} \left[ \begin{array}{ccc}
\rho_i \ln \rho_i & \rho_i & E_i \rho_i \\
\sum E_i \rho_i \ln \rho_i & \sum E_i \rho_i & \sum E_i^2 \rho_i \\
\sum E_i \rho_i & \sum E_i^2 \rho_i & \sum E_i^2 \rho_i
\end{array} \right].
\]  

(6.27)

The dissipation term in equation (6.26) or (6.27) moves the system’s entropy in the local direction of “steepest entropy ascent” (Beretta, 2009) at constant energy \( E = \sum_{i=1}^L \rho_i E_i \) and composition. This is expressed explicitly in terms of the time evolution of \( S = k \sum_{i=1}^L \rho_i \ln \rho_i \) by the entropy balance written as

\[
\frac{dS}{dt} = k \frac{1}{\tau} \left[ \begin{array}{ccc}
\sum \rho_i (\ln \rho_i)^2 & \sum \rho_i \ln \rho_i & \sum E_i \rho_i \ln \rho_i \\
\sum E_i \rho_i \ln \rho_i & \sum E_i \rho_i & \sum E_i^2 \rho_i \\
\sum E_i \rho_i & \sum E_i^2 \rho_i & \sum E_i^2 \rho_i
\end{array} \right].
\]  

(6.28)

where the entropy generation term to the right of the equals is always non-decreasing.

**6.2.4. Evolution in Time of the Thermodynamic State and Position**

Finally, with all the eigenvalues \( \rho_i \) of the state operator \( \rho \) known at each instance of time \( t \) and the system-level eigenfunctions \( u_i \) as a function of the spatial coordinates \( \bar{x} \), the probability distribution function \( \Phi(\bar{x}, t) \) for the evolution in time and space of the state of the hydrogen particles in the tank is found from

\[
\Phi(\bar{x}, t) = \sum_{i=1}^L \rho_i(t) |u_i(\bar{x})|^2
\]  

(6.29)
The first moment of this distribution function, used in the results presented below, is the mass density expressed as a function of time by

\[ \xi(t) = \iiint \Phi m_{H_2} n \, dV \]

where \( m_{H_2} \) is the mass of a hydrogen molecule and \( n \) the number of these molecules in the system.

### 6.3 Dealing with Large Numbers of Energy Eigenlevels: Coarse-graining

#### 6.3.1. Need for Coarse-graining

The complexity of solving the energy eigenvalue problem goes up markedly with the number of spatial dimensions considered (i.e., 1D, 2D, or 3D (Smith et al. 2010; Sciacovelli Smith, Verda, and von Spakovsky, 2008; von Spakovsky, Smith, and Verda, 2008; Smith and von Spakovsky, 2007)). Consequently, for the 3D calculations, eigensolutions spanning only a limited energy range are calculated because the codes developed and used here to date have only run on high-end PC workstations. Future work entails modifying and transporting the code to a massively parallel supercomputer. For the results presented here, however, only two hundred eigensolutions (\( M=200 \)) are calculated for each translational two-body problem. Despite this limited number, the total number of possible primitive levels turns out to be \( P = M^3 R = 200_{C-H_2} \times 200_{C-H_2} \times 200_{H_2-H_2} \times 15_{H_2\_rot} = 1.2 \times 10^8 \). If all of these are actually used so that \( M = P \), then for the case of \( N = 2 \), the number of system levels \( L \) as given by equation (6.14) explodes to something on the order of \( 10^{15} \). Obviously, for computational reasons, the number must be reduced to something more manageable, and this is done via the technique of coarse-graining the energy eigenlevels.

#### 6.3.2 Coarse-Graining and Rescaling

A coarse-graining scheme is used here in which bundles of many system energy eigenlevel occupation trajectories are replaced with single representative trajectories. Previous work (Smith et al., 2010; Sciacovelli et al., 2009) also used methods that amounted to coarse-graining in order to limit the number of levels. However, the method employed in the present work is done in a more systematic way with the underlying justifications being more carefully considered.
In the context of the work here, trajectories are traces that describe how the occupation probabilities of the energy eigenlevels of a system vary over time. They depict as a function of time the probability that a given energy eigenlevel will be occupied by the system. Figure 6.2 illustrates how the trajectories for energy eigenlevels that lie within a restricted energy range, i.e., within a so-called “bundle”, tend to evolve similarly in time and might, therefore, be replaced by a single, judiciously chosen trajectory. The computational burden can thereby be reduced while retaining the major dynamical characteristics of the system.

In order to help validate this coarse-graining technique, we compare the results of coarse-graining are compared to the exact solutions for a given sample system. This is possible as long as the number of trajectories is not too large. The maximum number of trajectories solved for to date on a high-end PC workstation has been on the order of a million. The exact results for a

![Figure 6.2. Solution of the IQT equation of motion for a set of energy eigenlevels over a limited energy range, i.e., for a so-called “bundle” of trajectories with energies close to one another and behaving similarly in time.](image)

Figure 6.2. Solution of the IQT equation of motion for a set of energy eigenlevels over a limited energy range, i.e., for a so-called “bundle” of trajectories with energies close to one another and behaving similarly in time.

system having this many or fewer trajectories are, thus, compared to our coarse-grained results. Provided the correlation between the coarse-grained and the exact solution for this limiting case is good, a reasonable assumption is that the coarse-grained results can be extrapolated to even higher numbers of levels for which exact solutions are not possible.

Figure 6.3 compares a set of trajectories from an exact solution with their coarse-grained counterparts. In order to compare the fewer number of coarse-grained trajectories with those for
the exact solution, the number of trajectories for the latter is reduced by averaging their effects over the same energy ranges used to determine the bundles for the coarse-grained trajectories. In Figure 6.3, the averaged trajectories of the exact solution are steeper than those for the coarse-grained solution, but the two sets of trajectories are seen to start at the same initial values and end at very near the same stable equilibrium values, thus, providing credence for the use of coarse-graining as an approximate method. Of course, there remains the question of the proper scaling of the magnitude of the coarse-grained solution since it necessarily underestimates that of the exact solution. This is addressed below.

As to determining the coarse-graining itself, the technique used is to divide the entire energy range for the full number of energy eigenlevels into bundles having an equal number of levels. The energy level having the median index (quantum number) within a given bundle is chosen as representative of that bundle. The coarse-grained levels, thus, reflect the overall density of levels for the larger system. Where the levels for the larger system are closely spaced or sparse, the coarse-grained approximation is also closely spaced or sparse.

![Figure 6.3. Coarse-grained and exact trajectories are compared in a normal (figure on the left) and a magnified (figure on the right) view; paired trajectories (coarse and exact) have the same color with the steeper slope indicating the trajectory from the exact solution and the gentler the coarse-grained one.](image)

The differences in trajectory slopes seen in Figure 6.3 indicate that coarse-graining introduces errors in magnitude that must be addressed if this technique is to be used to model larger systems. The number of trajectories affects for example, the magnitude of the entropy of
the system as well as the speed at which the system evolves towards stable equilibrium. Since the entropy for a given system energy is proportional to the natural log of the number of energy eigenlevels available to the system, the entropy of the coarse-grained system will necessarily be lower than that for the larger (i.e., exact) system. In addition, systems accessing a higher density of energy eigenlevels also evolve more quickly. These effects must be taken into account by properly scaling the coarse-grained results. If the scaling of the entropy and the time evolution of the coarse-grained system is correctly done, the overall changes in entropy and the occupation probabilities with time can be made to closely represent the behavior of the larger system.

Figure 6.4 illustrates how coarse-grained results are scaled to represent those of the larger system. In this figure, 20 energy eigenlevels representing the coarse-grained system are used to represent a system with 10,000 levels as illustrated by this diagram of entropy versus time. Proper scaling of the amplitude of the coarse-grained curve allows one to match the full range of entropy for the larger system. Furthermore, by compressing the time axis, the slope of the trace is steepened and the rate of time evolution is made to correspond to the large system. Finally, a time shift is required to place the approximate curve on top of the curve for the larger system. Slight deviations are seen between the actual curve and the approximate one, but with these three simple scaling procedures a surprisingly close correspondence is achieved.

Figure 6.4. Scaling example of how a small number of coarse-grained energy eigenlevels can closely approximate the collective behavior of many levels if proper scaling is used.
Figures 6.5 to 6.10 below provide relationships for the scaling factors for entropy, the time scale, and the time shift associated with the system depicted in Figure 6.1. Two sets of scaling factors are needed: one for the primitive energy eigenlevels representing one hydrogen pair followed by the other for the system energy eigenlevels representing two hydrogen pairs. It is apparent from the primitive level data in Figures 6.5 to 6.7 that all three of the scaling factors are proportional to the log of the number of primitive energy levels $M$ that are utilized in the simulation. In contrast, the system-level scaling for two hydrogen pairs as shown in Figures 6.8 to 6.10 is based on the expression

$$L = M(M+1)/2.$$  

**Figure 6.5.** Entropy scale factor as a function of primitive levels; the scaling factor is based on 200 coarse-grained levels.

**Figure 6.6.** Inverse of the time scale factor as a function of primitive levels; the scaling is based on 200 coarse-grained levels.

**Figure 6.7.** Time shift for 200 coarse-grained levels as a function of the number of primitive energy eigenlevels.

**Figure 6.8.** System-level entropy scaling factor as a function of the number of primitive levels for the case of $N=2$; the asymptotic limit is 2.
Since the number of system levels goes up geometrically instead of exponentially, the system-level scaling factors approach asymptotic values as \( M \) gets large.

The evolution data for the state of the system when initially calculated, are for \( L = 20,100 \) system levels that are based on \( M = 200 \) coarse-grained “primitive” energy eigenlevels that span \( 1.2 \times 10^8 \) energy eigenlevels for one pair of \( \text{H}_2 \) molecules. The actual number of system levels to be represented is \( 7.2 \times 10^{15} \). The entropy and time axis of the resulting entropy and state evolution results must, therefore, be scaled to represent the results for the higher numbers of energy levels.

The data for the 20,100 system levels have an intrinsic system scaling that must first be removed. The empirical relationships found in Figure 6.8 and Figure 6.9 are used for this purpose. The “backwards” scaling for entropy and time to 200 primitive levels based on Figures 6.8 and 6.9 is then,

\[
\langle S \rangle_{\text{scale,sys}} = \left( \ln(L) - \langle S \rangle_{\text{init}} \right) / \left( \ln(M) - \langle S \rangle_{\text{init}} \right)
\]

\[
t_{\text{scale,sys}} = 1.142 M^{-0.531} + 0.5
\]

where \( L \) is 20100, the number of system levels, \( M \) is the number of primitive levels and \( \langle S \rangle_{\text{init}} \) is the entropy value at \( t = 0 \). The scale value for the entropy of the present example was found to be 1.872 and the entropy data is divided by this number so that the entropy data is representative of 200 primitive levels. Likewise, based on Figure 6.9, the time scaling was found to be 0.506 and the time axis is divided by this factor to achieve the desired reverse scaling. A similar procedure is done for the time shift based on Figure 6.10. In actual practice the time shift is of

![Figure 6.9. System-level time scaling factor as a function of the number of primitive levels for the case of N=2; the asymptotic limit is 0.5.](image)

![Figure 6.10. System-level time shift as a function of the number of primitive levels for the case of N=2; the asymptotic limit approaches 0.25.](image)
conceptual interest and can be set to any convenient value, so further discussions for this factor are omitted.

Now the entropy data and time axis for the results can be scaled upward to represent $1.2 \times 10^8$ primitive levels. The empirical relationships of Figure 6.5 and Figure 6.6 are used, i.e.,

$$\langle S \rangle_{\text{scale_prim}} = 0.8604 \ln(M) - 5.1909$$

$$t_{\text{scale_prim}} = 1/(0.2026 \ln(M) - 0.1199)$$

where $M$ is the desired number, e.g. $1.2 \times 10^8$, of primitive energy levels to be represented. The scaling numbers for entropy and time are estimated to be 10.812 and 0.274 respectively. The entropy data values and time axis are multiplied by these scale factors.

Next the entropy and time axis must be scaled again to represent $L = 7.2 \times 10^{15}$ system levels. The numerical relationships associated with Figure 6.8 and Figure 6.9 are again used. The system scale factors are,

$$\langle S \rangle_{\text{scale_sys}} = \ln(M(M+1)/2)/\ln(M)$$

$$t_{\text{scale_sys}} = 1.142M^{-0.531} + 0.5$$

where $M$ is the number of primitive energy levels and the number of system levels $L$ is implied since $L = M(M+1)/2$. At very large $M$ values, the entropy and time scaling approach the asymptotic values of 2.0 and 0.5 respectively. The system level scaling obtained for the present results were found to be 1.963 and 0.50 for the entropy and the time axes respectively. The primitive and system scaling factors are multiplied together, which obtains overall scaling values of 21.22 and 0.137 respectively for the entropy data and the time axis. Once the overall entropy scaling has been applied, the offset value of $0.808 \times 1.38 \times 10^{-23}$ J/K for $\langle S \rangle_{\text{init}}$ is added back in to the entropy data.

In summary, the amount of entropy and speed of evolution are seen to increase as the logarithm of system size. The scaling factors serve to increase the entropy and compress the time axis of the test system of 20100 energy eigenlevels to allow the test system to emulate the behavior of a much larger system having many more energy eigenlevels.

### 6.3.3 Extended Coarse-Graining of the Translational Energy Levels

In the initial attempts to model hydrogen storage on a carbon nanotube in 3D using IQT theory (Smith et al., 2010; Sciacovelli et al., 2009), the magnitude of the highest energies of the
200 single-particle translational energy eigenlevels was only about $1/10^\text{th}$ the energy of the first rotational energy for hydrogen. As a consequence, large gaps are seen in the spectrum of the coarse-grained system energy eigenlevels. The translational energies are grouped closely around the incremental energy contributions of the rotational energy levels. A more detailed illustration of the phenomenon is shown in Section 1 of Chapter 7. It is thought that a more realistic model can be constructed if the translational energy levels are spread more evenly over the energy range between the translational ground state and the first rotational energy eigenlevel.

The scheme that was chosen calculates 200 translational eigenlevels and divides them into 10 groups of 20 eigenlevels each over the energy span to the first rotational energy level. The spacing between the groups is made proportional to the density of energy states, so that as energy increases the groups are more closely spaced than at lower energies. For a particle in an empty box, the density of states for translation goes as $g(E) \propto E^{1/2}$ similar to the density of states for a free electron gas, (e.g., Kittel, 2005). Numerical studies for the current work indicate a dependence closer to $g(E) \propto E^{1/4}$ for the box containing the nanotube. The choice for spacing is at best an estimate and was found to be similar whether $E^{1/4}$ or $E^{1/2}$ was used. Figure 6.11 illustrates the spacing between groups that was utilized. The number of single-particle transla-

![Figure 6.11](image)

**Figure 6.11.** The energy spacing of the eigenlevel groups based on $g(E) \propto E^{1/4}$ that was used for coarse-graining the spectrum of the translational eigenlevels up to the first rotational energy.

The number of single-particle transla-

...ional eigenlevels is the same as before, so the spreading out of the translational levels should not affect the coarse-grain scaling strategy for calculating the system entropy.
6.4 Numerical Approach

6.4.1. Numerical Approach for Solving the Energy Eigenvalue Problem for Translation

Each of the two-body eigenvalue problems for translation is numerically solved by the finite-element method (FEM). A proper weak formulation is used to apply FEM to this problem, namely,

\[ \int \nabla u \cdot \nabla \nu \, d\vec{x} + \int V(\vec{x})u \, \nu d\vec{x} = \epsilon \int u \nu d\vec{x} \]  

(6.38)

where \( \nu \) is the test function and \( \epsilon \) the eigenvalue considered. The solution \( u \) is approximated by second order Lagrange polynomials \( \varphi_j \), i.e.,

\[ u(\vec{x}) = \sum_{j=1}^{N_h} u_j \varphi_j(\vec{x}) . \]  

(6.39)

From Eqs. (6.38) and (6.39), the following generalized eigenvalue problem is deduced:

\[ \tilde{R} \tilde{u} = \epsilon \tilde{M} \tilde{u} \]  

(6.40)

where \( \tilde{u} = (u_j) \), \( \tilde{R} \) is the stiffness matrix, and \( \tilde{M} \) is the mass matrix, the elements of which are given by

\[ K_{ij} = \int \nabla \varphi_i \cdot \nabla \varphi_j d\vec{x} + \int V(\vec{x})\varphi_i \varphi_j d\vec{x} \]  

(6.41)

\[ M_{ij} = \int \varphi_i \varphi_j d\vec{x} . \]  

(6.42)

For the case of the center of mass (cm) problem, the potential is zero in which case the stiffness matrix becomes

\[ K_{cm,ij} = \int \nabla \varphi_i \cdot \nabla \varphi_j d\vec{x} . \]  

(6.43)

Matrices \( \tilde{R} \) and \( \tilde{M} \) are properly modified to match the boundary conditions, which for the simulation here requires the solution to be zero at the nodes that make up the walls of the box. The generalized eigenvalue problem is then solved by the Arnoldi algorithm (Arnoldi, 1951; Quarteroni, Sacco, and Saleri, 2000) applied to a shifted and inverted matrix with restarts until the eigenvalues are found. Solutions are considered converged after the residuals are less than \( 1.0 \times 10^{-6} \). The adopted grid consists of an unstructured mesh of 690,000 tetrahedral elements with 120,000 interior nodes to ensure a grid independent solution. Figure 6.12 illustrates an example of a mesh with the same dimensions as the nanotube-in-a-box system under study. The example contains only 4500 elements to show the mesh structure more clearly.
Once a mesh size has been chosen, the FEM algorithm is used to determine the desired eigenenergies and eigenfunctions by solving the time independent Schrödinger equation for the H$_2$ plus nanotube system as well as for the H$_2$-H$_2$ interactions. The numerical solution yields values for a given eigenfunction at each of the interior nodes of the mesh.

Graphics routines are used to interpolate the solution as needed, producing 3D renderings of a desired eigenfunction as shown in Figure 6.13. Areas of strong coloration indicate a large positive or negative amplitude of the eigenfunction and a higher probability of finding the hydrogen molecule in that region. The cylinder-shaped void in the vicinity of the carbon atoms of the nanotube is clearly seen. The pattern of the green and blue patches indicates a strong likelihood of finding the hydrogen inside the nanotube as well as on the outer surface.

The resulting solution data can also be used to illustrate the relative probability of finding a hydrogen molecule near the nanotube as a function of radial distance for a given eigenfunction as Figure 6.14 shows. The red dots represent the amplitude of the wave function as calculated for various mesh nodes within the box. The green trace is the square of the amplitude which indicates the relative probability of finding a hydrogen molecule a given distance from the center of the nanotube for the given eigenfunction. A radius of 7 Å or less is inside the tube while 13 Å and higher are exterior to it.
Figure 6.13. 3D rendering of an eigenfunction solution for a hydrogen molecule interacting with the carbon nanotube model under study.

The blue dots show the strength of the potential function of the nanotube which is calculated by a summation of the Lennard-Jones functions of each of the carbon atoms. The regions of negative values for the potential function tend to attract the hydrogen while areas of positive values very near the carbon atoms of the nanotube repel the hydrogen molecules. In order to get a complete picture of how hydrogen interacts with the nanotube, the entire set of eigenfunctions and eigenvalues for the $H_2$-nanotube, $H_2$-$H_2$ interactions as well as the contributions from the rotation of the hydrogen molecules need to be combined and displayed for various times as the system relaxes to stable equilibrium.

6.4.2. Numerical Approach for Solving the QT Equation of Motion

A system of 20,100 first order ordinary differential equations (ODEs) is generated from the IQT equation of motion and used to determine the evolution in state of the system. This system of equations is solved numerically forward and backwards in time using a Runge-Kutta 4,5 (RKF45) method, starting from an arbitrarily chosen dimensionless time of $t^* = -2.0$. The
Figure 6.14. Depiction of H$_2$ density (in green) versus radial distance from the center axis of the nanotube for a single eigenfunction. The result was calculated using the FEM for a H$_2$-nanotube interaction.

Runge–Kutta–Fehlberg method (Fehlberg, 1969, 1970; Hairer, Nørsett, and Wanner, 1993) uses a fourth order approach together with a fifth order one by employing all of the points of the former plus one additional calculation required by a Runga-Kutta 5 method. The RKF45 method is, thus, able to estimate and control the error in the solution and determine an appropriate step size automatically. This makes the method efficient for ordinary problems of automated numerical integration of ODEs.
Chapter 7 - Results and Discussion

Presented are the results from implementation IQT simulations for hydrogen storage on a carbon nanotube and for extensions of IQT theory to include heat and mass interactions. All of the results come from the original contributions of the present doctoral work. For the problem of hydrogen storage on a nanotube the most recent findings are compared to Smith et al., 2010 which uses a slightly different and less effective scheme for the coarse-graining of energy levels. The behavior of both models over time is examined, compared and discussed. Included are the probability density distributions, which show the relative density of the hydrogen around the nanotube as a function of time, as well as the solutions to the IQT equation of motion, graphs of system entropy and the time evolution of the density of energy states for each system. Also shown are illustrations of one-particle primitive eigenfunction for both C-H$_2$ and H$_2$-H$_2$ interactions. For the most recent simulations, results derived from IQT that show hydrogen density as a function of radial distance from the center of the nanotube are compared to similar results found in the literature derived from GCMC and MD models for stable equilibrium.

The discussion of the extension of IQT theory to heat interactions compares the effectiveness of BPHI operator implementation with the most recent rotationally based RPHI operator. The BPHI operator was derived by Beretta (2009a) while the implementation of the BHPI as well as the derivation and implementation of the RPHI are original contributions of this current work. The behavior, merits and drawbacks for each of the operators is discussed. Also shown are the results of fitting the BPHI operator to the experimental data of Turchette et al. (2000), which is included for comparison to the curves shown for the RPHI operator shown in Chapter 5.

Finally, data for the IQT based development and implementation of the rotational RPMI operator for mass interactions is presented. The construction of the open system energy levels with varying particle numbers is explained. The time evolution calculated from the RPMI operator together with the dissipation operator for an open system are shown for a simple system.
7.1 Non-equilibrium Evolution in State for Hydrogen Storage on a Carbon Nanotube

7.1.1 Initial Simulation Using Coarse-graining, Smith et al., 2010

Figures 7.1 to 7.4 show the evolution in time of the probability distribution function (Eq. (6.29)) for the system of Figure 6.1 comprised of four hydrogen molecules \((N=2)\) and the 900 carbon atoms that make up the carbon nanotube. The coarse-graining scheme for the system translational energy eigenlevels in this case spanned only about 10 percent of the energy interval to the first rotational energy of \(H_2\). The quantity \(t^*\) is a dimensionless time that has been rescaled to represent system with approximately \(10^{15}\) energy eigenlevels. At the initial (non-equilibrium) state at \(t^*=-2.0\), one can see in Figure 7.1 that the highest values of the probability distribution function and, therefore, the highest densities (the dark red) of hydrogen occur in and around the tube as well as away from the tube and towards the bottom wall of the tank. In Figure 7.2, this picture has evolved so that in this new non-equilibrium state at \(t^*=-0.224\), one can see a somewhat greater concentration of hydrogen inside the tube and nearer the outside tube walls.
The concentration of hydrogen near the bottom of the tank has also increased as has the hydrogen in the upper part of the tank.

From this last state, the state of the system evolves to the state shown in Figure 7.3. This new intermediate non-equilibrium state occurs at \( t^* = 0.4894 \). As can be seen in this figure, the state of the system has evolved to the point that the value of the probability distribution function and, thus, the density of hydrogen has significantly decreased at the bottom of the tank and concentrated even more in and around the carbon nanotube.

![Figure 7.3](image1.png) ![Figure 7.4](image2.png)

**Figure 7.3.** Plot of the probability density (probability distribution function) of particle position as a function of position at an intermediate non-equilibrium state at \( t^* = 0.4894 \) with \( N=2, M=200, \) and 20,100 system energy eigenlevels utilized.

**Figure 7.4.** Plot of the probability density (probability distribution function) of particle position as a function of position at stable equilibrium at \( t^* = 1.198 \) with \( N=2, M=200, \) and 20,100 system energy eigenlevels utilized.

Finally, Figure 7.4 shows the final state of the system in stable equilibrium at \( t^* = 1.198 \). As should be evident from the figure, the highest values of the probability distribution function and, thus, the hydrogen densities (the dark red) occur in the tube and close to the outer walls of the carbon nanotube. The temperature at stable equilibrium is about 28 K which means that the hydrogen quantum molecular model used here is consistent with a gaseous state for the hydrogen since hydrogen has a triple point temperature of 14 K at 0.07 atm.

Now, in order to assess the irreversibilities which occur during the thermodynamic process depicted in the previous figures, one can examine the rate of entropy generation as well
as the change in the entropy due to irreversibilities. Both are shown in Figure 7.5 and both results are scaled to represent the larger system with its $10^{15}$ system energy eigenlevels. The vast

![Image](image_url)

**Figure 7.5.** Evolution in time of the entropy (left) and the entropy generation rate (right). Both have been scaled to represent the results of the larger system with $10^{15}$ system energy eigenlevels.

majority of the entropy creation and, thus, the increase in the entropy of the system occurs in a time interval of $t^\# = 0.3$ to $t^\# = 0.6$. This corresponds with the largest number of energy eigenlevels coming into play, taking up a share of the overall system's energy and becoming occupied as the state of the system moves towards the stable equilibrium (canonical) distribution (see Figure 7.6). Note that the gaps in the energy eigenlevels seen in Figure 7.6 are due to the

![Image](image_url)

**Figure 7.6.** Normal (figure on the left) and magnified (figure on the right) views of the evolution in time of the 20,100 coarse-grained energy eigenlevel trajectories; the trajectories represent simultaneous solutions to the IQT equation of motion.

fact the these particular results are based on a set of translational eigenvalues ($M=200$ currently) which do not fully span the energy range up to the lowest rotational energy eigenlevel.
In order to view the evolution in state of the system in another more traditional light, the probability density distribution of energies is calculated for the non-equilibrium states through which the system passes as well as for the stable equilibrium state at which the system arrives. The results for the latter state and for two of the three non-equilibrium states are shown in Figure 7.7. As can be seen, there is an evolution from a non-Maxwellian type of distribution at $t^* = -2.0$ and at $t^* = 0.224$ to a Maxwellian type of distribution at stable equilibrium. This is what one would expect, but what is significant here is that one does not have to guess at the distributions since they fall directly out of the physics/thermodynamics of the problem captured by both the IQT equation of motion and the energy eigenvalue problem associated with the behavior of the hydrogen molecules relative to each other and to the carbon atoms in the tank. As in Figure 7.6, the gaps in the distribution occur due to the fact that the set of primitive translational eigenvalues used ($M=200$ currently) do not fully span the energy range up to the lowest rotational energy eigenlevel.

Finally, to determine the minimum number of finite energy eigenlevels required for modeling the evolution of state of the system to an acceptable level of accuracy, a plot of the system energy $\langle E \rangle$ versus the system entropy $\langle S \rangle$ is made for different numbers of eigenlevels including the so-called limit curve of an infinite number of levels. The results are shown in Figure 7.8 along with the maximum thermodynamic temperature at which the accuracy for a given number of finite energy eigenlevels begins to decrease. As is seen, with 20,100 coarse-grained system energy eigenlevels utilized, the system can be modeled with good results for temperatures at stable equilibrium up to about 28 K. After that, the stable equilibrium curve for 20,100 levels begins to diverge significantly from the limit curve which is based on an infinite number of levels. To achieve higher temperatures, more system energy eigenlevels must be
used. It should also be emphasized here that the thermodynamic temperature only has meaning at stable equilibrium and is not defined for non-equilibrium states. This, however, unlike in other approaches (e.g., MD), poses no problem for describing the thermodynamic evolution of state of the system since the IQT equation of motion does not require it.

Figure 7.8. Expectation energy $\langle E \rangle$ versus the expectation entropy $\langle S \rangle$ for the hydrogen in the 3D tank with $N=2$ and $M=200$ and the number of coarse-grained system energy eigenlevels varying between 100 and 20,000.

7.1.2 Results for Extended Coarse-Graining of the Translational Eigenlevels

Section 6.3.3 of Chapter 6 discusses an alternate simulation that is run using additional coarse-graining of the single-particle translational energy eigenlevels. The 200 translational eigenlevels are spread out in ten groups of 20 eigenlevels each over the range from the ground state to the energy of the first $H_2$ rotational energy eigenlevel. The intent is that the wider spread of energy due to the additional coarse-graining will produce a more realistic model and avoid the large energy gaps seen in Figure 7.6 that were produced by the narrower range of translational energy eigenlevels.

Figures 7.9 and 7.10 show examples of the translational single-particle eigenfunctions for the $H_2$-nanotube interactions that are used, together with the $H_2$-$H_2$ eigenfunctions, to form the eigenfunctions for the system. As is evident, the lowest of the $H_2$-nanotube eigenfunctions shows a marked affinity between the hydrogen molecules and the nanotube. The areas of high contrast with respect to the background of the figures correspond to areas where it is more likely to find the hydrogen, and are seen to be near or inside the nanotube. For higher energies, how-
Figure 7.9. Examples of single-particle eigenfunctions for the interaction of H\textsubscript{2} with the carbon nanotube. A low energy example is on the left and a higher energy example is on the right.

Figure 7.10. Examples of single-particle eigenfunctions for the hydrogen-hydrogen interactions. A low energy example is on the left and a higher energy example is on the right.

However, the attraction between nanotube and the H\textsubscript{2} molecules is seen to be much weaker, as is expected. The areas of contrast have a higher spatial frequency (are smaller and more numerous) and are spread more or less evenly throughout the box.

The single-particle eigenfunctions for the H\textsubscript{2}-H\textsubscript{2} interactions are shown in Figure 7.10. The areas of higher probability are spread throughout the box, with those of higher energies having a higher spatial frequency. It would appear that although the H\textsubscript{2}-H\textsubscript{2} interactions contribute to the system eigenenergies, their eigenfunctions have little effect with regard to
finding H\(_2\) near the nanotube. The only apparent effect is to include higher frequency components to the system eigenfunctions.

In general, Figures 7.9 and 7.10 show that sets of one-particle eigenfunctions that are spread out over a wider range of energy should cause the attraction of the nanotube for hydrogen molecules to appear weaker. The higher the energy the less the H\(_2\) molecules are attracted to the nanotube, so the higher energy eigenfunctions do not contribute much to finding the hydrogen near the nanotube. However, a strong argument for using this additional coarse-graining technique is that the resulting model is more representative of the actual range of energies that would affect the amount of hydrogen storage on a nanotube.

Figures 7.11 to 7.14 show the evolution in time of the probability distribution function with the additional coarse-graining scheme for the translational eigenenergies. The red-colored regions show areas with the greatest H\(_2\) concentrations. The sequence of figures shows an unmistakable increase in hydrogen concentration near or inside the nanotube with time, even though the 200 translational eigenfunctions used in the coarse-graining procedure span an energy

![Figure 7.11](image.png)

**Figure 7.11.** Plot of the probability density distribution at the initial non-equilibrium state for hydrogen with respect to the carbon nanotube at \(t^* = -0.03\) for the coarse-grained translational eigenlevels.
Figure 7.12. Plot of the probability density distribution at the initial non-equilibrium state for hydrogen with respect to the carbon nanotube at \( t^* = 0.22 \) for the coarse-grained translational eigenlevels.

Figure 7.13. Plot of the probability density distribution at the initial non-equilibrium state for hydrogen with respect to the carbon nanotube at \( t^* = 0.37 \) for the coarse-grained translational eigenlevels.
Figure 7.14. Plot of the probability density distribution at stable equilibrium for hydrogen with respect to the carbon nanotube at $t^* = 1.41$ for the coarse-grained translational eigenlevels.

range that is ten times greater than in the previous simulations.

The evolution of system density, entropy and entropy generation rate is shown graphically in Figures 7.15 to 7.17. As with the previous simulations, the results are scaled to represent the larger system with its $10^{15}$ system energy eigenlevels. Using the methods discussed in Chapter 6, the range of entropy from minimum to maximum has been multiplied by a scaling factor of 11.34 while the time axis has been compressed by a factor of 3.61. Even though the translational energy eigenlevels have been spread over a wider range of energy, the number of resulting system eigenlevels is the same as before. The scaling of the entropy therefore is not affected by coarse-graining of the translational eigenlevels, yielding similar results for entropy change and entropy production rate as the results discussed in Section 7.1.1.

The density of hydrogen storage for the interior of the carbon nanotube as a function of time is shown in Figure 7.15. Initially it is seen that very little hydrogen is found inside the tube. The density is near 0.0535 kg/m$^3$, which is the average density for four H$_2$ molecules within the entire system boundary. As stable equilibrium is reached, the tube density goes up markedly, by a factor of almost 20, due to the attraction of the hydrogen for the nanotube. The final density is near 1.155 kg/m$^3$, the simple mass/volume density for four H$_2$ molecules in the interior of the nanotube. Since the simulation uses only four hydrogen molecules, it is not yet possible to esti-
Figure 7.15. Mass density of $\text{H}_2$ within the interior of the carbon nanotube as a function of time.

Figure 7.16. Evolution in time of the entropy (right) and entropy generation rate (left). Both have been scaled to represent the results of the larger system with $10^{15}$ system energy eigenlevels.

mate the maximum density of hydrogen storage that could be achieved. The rate of entropy generation as well as the change in the entropy due to irreversibilities are shown in Figure 7.16.

The evolution of the state matrix which illustrates how the relative probabilities of finding the system in a given energy level as a function of time is shown in Figure 7.17. The details of the close-up view in Figure 7.17 b) are in marked contrast to Figure 7.6 of the previous study. It is seen that the coarse-graining of the translational energy levels has effectively filled the energy gaps seen in Figure 7.6.
Figure 7.17. The a) unexpanded and b) close-up views of the trajectories of the state matrix as calculated from the IQT equation of motion using the extended coarse-graining scheme.

Figure 7.18. Plot of the probability density distribution of energies at times $t^* = 0.13$, $t^* = 0.25$, $t^* = 0.60$ and $t^* = 1.44$ for the IQT simulation using the extended coarse-grained translational eigenlevels.
The evolution of the density of states distribution for the new coarse-grained case also shows in Figure 7.18 as expected a much more even distribution of energy eigenlevels. This is in marked contrast to the results of Figure 7.7. The initial state of the system are seen as a few energy levels with very high probability which appear as tall columns in the figures. As energy redistribution takes place, the probabilities of the initial energy eigenlevels diminish, while the other energy eigenlevels become more prominent.

Figure 7.19. Energy vs entropy curves for model systems with various numbers of energy levels. The greater the number energy levels the higher the equilibrium temperature that can be modeled.

A plot of the system energy $E$ versus the system entropy $S$ for various number of system energy eigenlevels is shown in Figure 7.19. The extended coverage of the translational energy levels has produced smoother curves than in Figure 7.8 for the earlier model. The largest accurate temperature that can be modeled for a system using 20,000 system eigenlevels is estimated to be in the low 20 K temperature range.

7.1.3 Comparison of IQT Results for H$_2$ Storage with Monte Carlo and Molecular Dynamics Methods

There have been experiments that have measured the amount of hydrogen storage on carbon nanotubes and other properties, e.g., (Lee et al., 2000). Most of the attempts to visualize the concentration of H$_2$ around nanotubes have come from numerical simulations. Three of the most prevalent techniques have been Density Functional Theory (DFT), e.g., (Lee and Lee, 2000; Cabria, Lopez and Alonso, 2006; Han and Lee, 2004), Grand Canonical Monte Carlo
methods (GCMC) (Rzepka, Lamp and Casa-Lillo, 1998; Wang and Johnson, 1999; Luo and Lloyd, 2009; Gu et al., 2001; Zheng, Wang and Cheng, 2004; Meregalli and Parrinello, 2002), and Molecular Dynamics (MD) simulations (Banerjee, 2008; Knippenberg, Stuart and Cheng, 2008; Cheng et al., 2005; Maruyama and Kimura, 2000; Dodziuk and Dolgonos, 2002). Of the three techniques GCMC and MD are seen to provide density profiles of hydrogen as a function of distance from the nanotube walls. Moreover, only MD can model a system out of equilibrium as it relaxes to stable equilibrium. There do not appear to be any experiments that have attempted to measure the concentration of hydrogen as a time-dependent process.

Figure 7.20 shows the likelihood of finding the H$_2$ molecules near the nanotube wall as a function of radial distance from the tube center for various times using the current IQT model. To avoid end effects, only the center 2/3 of the nanotube is used to collect the data. The initial state consists of 5 system energy eigenlevels that are occupied and arbitrarily chosen. It is seen that this method of selecting the initial state still leaves the nanotube with a pronounced concentration of H$_2$ near the outside surface instead of a more even distribution as is intended. Nevertheless, the figures show that over time significant evolution does take place and the hydrogen is increasingly likely to be found in the center of the tube as well as the outside wall as would be expected.

The H$_2$ density results for Wang and Johnson (1999) are shown in Figure 7.21 where they used GCMC techniques for the study of 3D nanotubes. In Figure 7.21a) the hydrogen distribution is depicted within an (18, 18) nanotube which is similar in diameter to the (15, 15) in the present research. Figure 7.21 b) depicts the interior and exterior concentration of H$_2$ of a narrower (9, 9) nanotube. The work of Rzepka and Lamp (1998) in Figure 7.22 uses sheets of carbon lattice. Knippenberg, Stuart and Cheng (2008) provide (see Figure 7.23) one of the few graphical representations of hydrogen density near nanotubes, in this case a bundle of three tubes, using the MD technique. Most MD studies give pictorial views of the positions of H$_2$ molecules which makes comparisons to the IQT results rather difficult. Pressures typically range from 5 MPa as in Wang and Johnson (1999) to 10 MPa as in Rzepka and Lamp (1998) with temperatures typically around 77 K. In Knippenberg, Stuart and Cheng (2008), the temperature is 300K but pressure is not specifically mentioned, only various loadings of hydrogen near the
Figure 7.20. Radial density of hydrogen with respect to the (15,15) carbon nanotube at times $t^* = 0.12$, $t^* = 0.25$, $t^* = 0.46$ and $t^* = 1.41$ for the IQT simulation. The density of $H_2$ is in magenta and the Lennard-Jones potential for the nanotube-hydrogen system is in blue. The tube radius is 10.17Å.

nanotube that were available for storage. However, in an interesting note, the relaxation time for their MD simulation is stated to be approximately 50 ps, which provides an estimate for the time constant of the IQT equation of motion.

For the IQT simulation containing just four $H_2$ molecules, a rough estimate of the pressure can be obtained by the ideal gas law,

$$p = \frac{Nk_BT}{V}$$

(7.1)
where $p$ is the pressure, $N$ is the number of particles, $k_b$ is Boltzmann’s constant, $T$ is the temperature and $V$ the volume of the box containing the nanotube. The pressure at $T=20$ K is found to be very low at around 4.4 kPa.

Qualitatively it is seen that all simulations, IQT included, produce similar positioning and width of the peaks of $\text{H}_2$ concentration near the carbon lattice. The IQT result shows at least a trace of small side lobes next to the main peaks as is seen for the GCMC and MD simulations.

![Graph](image)

**Figure 7.21.** Grand Canonical Monte Carlo results of Wang and Johnson (1999) for radial density of hydrogen storage on a) a 3D (18, 18) nanotube from an array and b) an isolated 3D (9, 9) nanotube. The units of $r^*$ are not apparent, but the radii of the (18, 18) and (9, 9) nanotubes are known to be 12.21 Å and 6.10 Å respectively. Used with permission, Am. Inst. Physics.

The IQT result also indicates equilibrium concentrations within the tube to be significantly greater than on the outer surface is as also shown in Wang and Johnson (1999). The average density value in and immediately around the tube for the IQT results though seemingly similar to that seen in Figures 7.21 to 7.23 cannot be directly compared since the number of particles in the latter is unknown, but certainly greater than the 4 particles used in the IQT simulation. Work is on-going to take the IQT system and simulate it with MD to provide a more relevant comparison.

### 7.2 Non-Equilibrium Evolution in State of a System Undergoing a Heat Interaction

Presented are typical results that were achieved after implementing the BHPI as well as RPHI operator terms in the IQT equation of motion. rotationally transformed version of a heat

Figure 7.23. MD results from Knippenberg, Stuart and Cheng (2008) showing radial density of H\textsubscript{2} with respect to the carbon nanotube. The different traces represent varying initial amounts of hydrogen in the system. Used with permission, Springer.

interaction. Both types are phenomenological in that the reservoir is treated as a separate system whose internal details are unknown except for the temperature at the interface with the system which is constant. Some of the cases show results for the BPHI and RPHI operators without an
internal dissipation term. Most examples include the effect of the internal dissipation operator term since this produces a more physically relevant model.

### 7.2.1 Heat Interaction Operator Based on the BPHI Formulation

An example of results of our implementation of the BPHI operator term developed by Beretta is shown in Figures 7.24 to 7.27. The case shown is for a 5 energy eigenlevel system which moves from a non-equilibrium state to mutual stable equilibrium with a reservoir of $T_R = 0.33$. The reservoir temperature is the slope at a given point along the $\langle E \rangle - \langle S \rangle$ stable equilibrium curve. Both the interaction and internal dissipation effects are present with the relative strengths of each being inversely proportional to $\tau_D = 1$ and $\tau_Q = 1.67$ for the two effects, respectively. Examples of straight trajectories with the internal dissipation operator term excluded are shown in Chapter 4. In addition, the results of fitting the BPHI to the experimental data of Turchette et al. (2000) is also shown and can be compared with the results from the RPHI version of the IQT equation of motion found in Chapter 5.

From Figure 7.24 it is seen that the implementation of the equation of motion with the BHPI dissipation terms is able to capture the curved paths that result from the effects of internal

![Figure 7.24](image-url). $\langle E \rangle - \langle S \rangle$ diagram showing the trajectories resulting from the equation of motion with the BPHI and dissipation terms for reservoir temperatures.
dissipation and various heat reservoir temperatures. As expected, the arcs of the curves for the most part are in the direction of maximum entropy. The curve for \( T_R = 0.1 \) however, is anomalous since it initially arcs away from the direction of increasing entropy. The trajectories for the negative \( T_R \) values cross each other, which also seems suspect. More investigation will be needed to determine the reasons for these unexpected behaviors.

Figure 7.25 shows that the state matrix for the system as a function of time can be successfully calculated using this form of the equation of motion. The pictured results come from using the Helmholtz version of these operators because it was found to be more stable numerically.

The changes in entropy for the system are shown in Figure 7.26 and are presented with reference to the basic entropy balance given by,

\[
\frac{S_{sys}}{T_R} = \frac{\dot{Q}}{T_Q} + \dot{S}_{irr} = \frac{\dot{Q}}{T_Q} 
\]

or

\[
\Delta S_{sys} = \frac{Q}{T_R} + S_{irr}
\]

Figure 7.25. The evolution of the state matrix as resulting from the equation of motion with the BPHI and dissipation terms for the case of \( T_R = 0.33 \).
In Figure 7.26, the quantity $\Delta S_{sys}$ is the overall change in system entropy, $S_{irr}$ is the amount of entropy generated during the interaction and $Q/T_R$ is the amount of entropy crossing the system boundary to the reservoir. The entropy transfer $Q/T_R$, since it is out of the system, is negative. The overall entropy change $\Delta S_{sys}$ for the system is positive. The curved $\langle E \rangle - \langle S \rangle$ trajectories of Figure 7.24 imply that the entropy change for the system is not always monotonic but may increase and decrease as stable equilibrium is reached as Figure 7.26 shows.

![Graph showing system entropy and related quantities over time](image)

**Figure 7.26.** For the case of $T_R = 0.33$, the change in system entropy, the amount generation and the amount of entropy transfer as a function of time resulting from the equation of motion with the BPHI and internal dissipation operator terms.

For interest, the evolution of the non-equilibrium temperatures $\theta_Q$, $\theta_H$, and $\theta_S$ are shown in Figure 7.27. These quantities have been defined in terms of ratios of variances and covariances between the energy and entropy of the system as shown in Chapter 3. The physical significance of these temperatures, if any, is not at present known. They are useful for putting the expressions for IQT dissipation and heat interaction operators into the more convenient Massieu or Helmholtz forms. All three quantities are seen to converge to the reservoir temperature.

The results from the IQI simulations with the BPHI and internal dissipation terms are compared with the experimental data of Turchette et al. (2000) in Figure 7.28. Details of the ex-
Figure 7.27. Illustration showing how the non-equilibrium temperatures $\theta_Q$, $\theta_H$, and $\theta_S$ of the BPHI and dissipation operator terms converge to the reservoir temperature $T_R = 0.33$.

Experiment are also given in Chapter 5 where comparisons to the data are made using the IQT RPHI and internal dissipation terms. The fit of the curves to the data is reasonably close, for the most part being within the limits of experimental uncertainty. There are however singularities encountered in the model near the time $t = 0.1$ that result in an abrupt drop-off right before stable equilibrium is reached.

7.2.2 Heat Interaction Based on the RPHI Formulation

The implementation of the RPHI operator term in the IQT equation of motion is straightforward. The pictured example, seen in Figure 7.30 is for a five energy eigenlevel system. When the internal dissipation is excluded, the expected behavior of straight trajectories connecting initial and final points is readily obtained. When the internal dissipation term is included (see Figure 7.31), plausible curved paths are the result. One weakness is numerical in nature and is seen when the dissipation term effect is much stronger than the effect of the heat interaction. In these cases, the trajectories approach the stable equilibrium curve so closely that they stop short and do not continue along the stable equilibrium curve to the heat reservoir point. This, however, is clearly only a numerical problem and not something fundamental with the equation.
Figure 7.28. Results of fitting the IQT simulations with the BPHI and internal dissipation terms to experimental data for a Be$^+$ ion in a Paul trap for the superposition states a) $|1\rangle$, b) $|2\rangle$ and c) $|3\rangle$ found in Turchette et al. (2000). The data show the decay of the state as a function of time after attaching an external heat reservoir. Data points are from Turchette et al. (2000) used with permission from the American Physical Society, copyright 2000.
Figure 7.29. $\langle E \rangle - \langle S \rangle$ diagrams of solutions of the IQT equation of motion equation having only an RPHI operator with reservoirs of various temperatures.

Figure 7.30. $\langle E \rangle - \langle S \rangle$ trajectories for the IQT equation of motion with RPHI and internal dissipation terms and with reservoirs at various temperatures. For the simulations, $\tau_D = 1.0$ and $\tau_Q = 1.67$.

Figure 7.29 shows a selection of trajectories calculated with just the RPHI operator term for various heat reservoir temperatures. As expected, each trajectory is straight and moves
directly to stable equilibrium with the reservoir at a point with the appropriate temperature on the stable equilibrium curve.

Trajectories in the $\langle E \rangle - \langle S \rangle$ plane for the system undergoing the effects of both the RPHI and internal dissipation terms are shown in Figure 7.30. The dissipation effect causes the path of evolution to bend out along the entropy axis as the system moves toward mutual stable equilibrium with the external heat reservoir. The relative strengths of the two effects are given by $\tau_D=1.0$ and $\tau_\varphi=1.67$, respectively. The trajectories are free of the anomalies for low and negative temperatures that are seen for the BPHI case.

![Figure 7.30](image)

**Figure 7.30.** Evolution based on the RPHI operator term alone for the density matrix of a 5-level system undergoing an interaction with a heat reservoir at a temperature of $T_R = 0.33$.

Figure 7.31 shows evolution of the state or density matrix with time as the system interacts with a heat reservoir at a temperature $T_R = 0.33$. The change of system entropy according to the entropy balance, equation (7.3), for $T_R = 0.33$ is shown in Figure 7.32. The entropy transfer $Q/T_R$, since it is going out of the system, is negative. The overall entropy change $\Delta S_{sys}$ for the system is positive as is indicated also by Figure 7.32. The non-equilibrium temperatures $\theta_H$ and $\theta_S$ are shown in Figure 7.33 where it is seen that they converge to the reservoir temperature $T_R$ when stable equilibrium is reached.

![Figure 7.31](image)
Figure 7.32. Change of system entropy, total entropy generation and entropy transfer entropy as a function of time for a system undergoing a heat interaction with a heat reservoir at $T_R = 0.33$. The evolution in state is based on the RPHI operator only.

Figure 7.33. The non-equilibrium temperatures $\theta_Q$ and $\theta_H$ of the IQT equation of motion with the RPHI operator term only.
Figure 7.34. Evolution based on the RPHI and internal dissipation terms of the density matrix of a 5-level system undergoing a heat interaction with a heat reservoir at $T_R = 0.33$.

Figure 7.35. Changes of system entropy, total entropy generation and the amount of entropy transfer as functions of time for a system undergoing a heat interaction with a heat reservoir at $T_R = 0.33$. The simulations are based on BPHI and internal dissipation terms.
Figures 7.34 and 7.35 show the evolution of the state matrix and the entropy change for the system as functions of time for the $T_R = 0.33$ trajectory. The entropy change for the system is seen to decrease somewhat as would be expected by noting the corresponding path in Figure 7.30 which curves back to a state of lower entropy. Again of interest are the non-equilibrium temperatures $\theta_Q$ and $\theta_H$ shown in Figure 7.36. The corresponding fit of the RPHI model with the internal dissipation term to the trapped ion data of Turchette et al. (2000) is presented in Chapter 5 and shows less of an abrupt drop-off in the trajectories as compared to the BPHI model with dissipation term.

### 7.2.3 Discussion of the RPHI Operator

The previous figures show that there is a close similarity in results achieved between the BPHI and RPHI operators. Experience has shown, however, that the rotational version has several practical advantages. There are fewer encounters with singularities and problems dealing with the quantity $\theta_Q$ are avoided. A broader range of reservoir temperatures can be modeled. Hence, solutions for interactions with reservoirs at temperatures near absolute zero can readily be
obtained. The rotational version is clearly based on a generalized rationale of steepest entropy ascent which gives it a conceptual advantage over the BPHI version. In addition, the fit of the IQT equation of motion based on the RPHI and the internal dissipation terms with experimental data appears to be better and the drop-off effect right before stable equilibrium which is seen in Figure 7.28 is much less severe. Going forward, the drop-off effect clearly requires explanation. Though likely numerical in origin, the possibility does exist of a physical basis for this effect.

7.3 Non-Equilibrium Evolution in the State of a System Undergoing a Mass Interaction

For an initial test of the effectiveness of the proposed IQT mass interaction operator developed in Chapter 4, a simple system containing a maximum of two atoms is used. The system is assumed to allow the passage of particles in or out across the system boundary, but its walls are “solid” enough to enable a discrete set of energy eigenlevels for the system to exist. The mechanism for the system permeability is not specified. Mass exchange with a mass reservoir could be due to such effects as tunneling, nanopores in the walls, or a larger hole within one or more of the walls. Only one chemical species of indistinguishable particles is used. For simplicity, the energy range of interest is limited to six energy eigenlevels that are equally spaced in energy except for cases of degeneracy.

In addition to the Hamiltonian operator which returns energy eigenvalues as a result of energy measurements of the system, there is the need for a number particle operator which returns the eigennumber of particles found in the system when the number of particles is measured. The number particle operator is implemented as a diagonal matrix similar to the Hamiltonian operator but with various particle eigennumber along the diagonal instead of eigenenergies. For simplicity, the system eigenfunctions are constructed by the multiplication of single particle eigenfunctions together while the system eigenvalues are found by summing the values of single particles as in Chambers (1991) and Hatsopoulos and Gyftopoulos (1977). The method is the same as was implemented for the investigations herein of hydrogen storage on a carbon nanotube except that particle number is now allowed to vary. The resulting eigenfunctions for the system containing two particles are constructed from the eigenfunctions for each particle so that
\[ u_{ij} = u_i^{(1)} u_j^{(2)} \]  \hspace{1cm} (7.4)

where \( u_{ij} \) is a system eigenfunction and \( u_i^{(1)} \) and \( u_j^{(2)} \) are the eigenfunctions for energies \( i \) and \( j \) of particles (1) and (2). The composite Hamiltonian \( H \) for the system then becomes,

\[ H = H^{(1)} + H^{(2)} \]  \hspace{1cm} (7.5)

where \( H^{(1)} \) and \( H^{(2)} \) are the one-particle Hamiltonians for the particles (1) and (2). It is also understood that a one-particle Hamiltonian can operate only on eigenfunctions of its corresponding particle. Similar relationships hold for \( N \), the particle number operator for the system.

Table 7.1 below illustrates how the system eigenfunctions \( u_{ij} \), the system energy eigenvalues, and the system particle number eigenvalues are constructed for the simple test system based on the eigenstates of particle (1) and particle (2). Energies span from 0 to 4 and are associated with a range of 0 to 2 particles. The two energy eigenlevels that have energies of 2 are degenerate.

Table 7.1. Construction of the open system energy levels with varying particle numbers.

<table>
<thead>
<tr>
<th>Eigenfunction</th>
<th>e.level schem.</th>
<th>Outcomes of energy measurements</th>
<th>( E ) e.v.</th>
<th>Outcomes of particle measurements</th>
<th>( N ) e.v.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_{00} = u_0^{(1)} u_0^{(2)} )</td>
<td>( ____ )</td>
<td>( Hu_{00} = H^{(1)} u_{00} + H^{(2)} u_{00} )</td>
<td>0</td>
<td>( Nu_{00} = N^{(1)} u_{00} + N^{(2)} u_{00} )</td>
<td>0</td>
</tr>
<tr>
<td>( u_{10} = u_1^{(1)} u_0^{(2)} )</td>
<td>( ___o )</td>
<td>( Hu_{10} = H^{(1)} u_{10} + H^{(2)} u_{10} )</td>
<td>1</td>
<td>( Nu_{10} = N^{(1)} u_{10} + N^{(2)} u_{10} )</td>
<td>1</td>
</tr>
<tr>
<td>( u_{20} = u_2^{(1)} u_0^{(2)} )</td>
<td>( o___ )</td>
<td>( Hu_{20} = H^{(1)} u_{20} + H^{(2)} u_{20} )</td>
<td>2</td>
<td>( Nu_{20} = N^{(1)} u_{20} + N^{(2)} u_{20} )</td>
<td>1</td>
</tr>
<tr>
<td>( u_{11} = u_1^{(1)} u_1^{(2)} )</td>
<td>( ___o )</td>
<td>( Hu_{11} = H^{(1)} u_{11} + H^{(2)} u_{11} )</td>
<td>2</td>
<td>( Nu_{11} = N^{(1)} u_{11} + N^{(2)} u_{11} )</td>
<td>2</td>
</tr>
<tr>
<td>( u_{21} = u_2^{(1)} u_1^{(2)} )</td>
<td>( o___ )</td>
<td>( Hu_{21} = H^{(1)} u_{21} + H^{(2)} u_{21} )</td>
<td>3</td>
<td>( Nu_{21} = N^{(1)} u_{21} + N^{(2)} u_{21} )</td>
<td>2</td>
</tr>
<tr>
<td>( u_{22} = u_2^{(1)} u_2^{(2)} )</td>
<td>( o___ )</td>
<td>( Hu_{22} = H^{(1)} u_{22} + H^{(2)} u_{22} )</td>
<td>4</td>
<td>( Nu_{22} = N^{(1)} u_{22} + N^{(2)} u_{22} )</td>
<td>2</td>
</tr>
</tbody>
</table>

The second column of the table illustrates schematically how the system energy eigenlevels are formed from the single particle eigenlevels. The lowest lines in each cell represent the lowest energy levels for each of the two individual particles, while the higher lines represent the next highest energy levels. A small circle over a line indicates whether a given
single particle energy eigenlevel is occupied. The system levels consist of varying combinations of the single particle levels keeping in mind that the particles are identical and indistinguishable. As a consequence, for example, a system eigenfunction $u_{12}$ would not be distinguishable from $u_{21}$ and so is not identified with a separate eigenstate. To determine the energy an energy eigenstate on the table, the single-particle energy for particle 1 is added to the single particle energy for particle 2. A similar relationship holds for determining particle eigenvalues shown in the last column of Table 7.1.

The IQT equation of motion with the RPMI operator term only, is implemented in the form of a Massieu function as discussed in Chapter 4. The RPMI operator is oriented along a desired direction in $\langle E \rangle - \langle S \rangle - \langle N \rangle$ space toward the stable equilibrium point in mutual stable equilibrium with the mass reservoir. The RPMI enables the system energy, mass and entropy to change along a maximal gradient path. Without the influence of the internal dissipation term solving the IQT equation of motion using the RPMI operator should produce a linear trajectory from the initial point to the final point at mutual stable equilibrium with the mass reservoir.

Figure 7.37. Linear trajectories to various mutual stable equilibrium points in $\langle E \rangle - \langle S \rangle - \langle N \rangle$ space for the evolution in state of a simple 2-particle, 6-energy eigenlevels system resulting from the IQT equation of motion with the RPMI term. The initial point is marked by a circle and $\tau_M = 1.0$.

Figure 7.37 shows that straight trajectories are indeed successfully produced by the proposed RPMI operator. The traces extend from an initial point to several points on the surface.
Figure 7.38. Evolution in state of the 2-particle, 6-eigenlevel open system with varying strengths of the internal dissipation and with the strength of the RPMI term based on a $\tau_M = 1.0$.

Figure 7.39. Trajectory to stable equilibrium of a simple system modeled with both the internal dissipation and RPMI terms. The blue curve is the projection of the 3D stable equilibrium surface onto the $\langle E \rangle - \langle S \rangle$ plane.
Figure 7.40. An alternate view of the trajectory of Figure 7.39 with respect to the stable equilibrium surface.

Figure 7.41. A view looking down on the $\langle E \rangle - \langle S \rangle$ plane of the trajectory of Figure 7.39.

of stable equilibrium states for the 3 dimensional $\langle E \rangle - \langle S \rangle - \langle N \rangle$ space. The horizontal trace having constant energy and particle number is a valid case for a mass interaction but also can be generated by the internal dissipation operator for an open system. The two types of interactions
are distinguishable and differ only by their time constants. Because the system is limited to 6 energy eigenlevels and 2 particles, the stable equilibrium surface curves back on itself in both the directions of energy and particle number. Though not depicted, the stable equilibrium surface should extend to the \( \langle E \rangle - \langle N \rangle \) plane.

Each terminal point of a trajectory represents a different mass reservoir and hence a different value for enthalpy per particle \( h_{M_R} \) and entropy per particle, \( s_{M_R} \), i.e.,

\[
\begin{align*}
h_{M_R} &= \frac{d\langle H \rangle_{\text{res}}}{d\langle N \rangle_{\text{res}}} = \frac{d\langle H \rangle}{d\langle N \rangle} \\
s_{M_R} &= \frac{d\langle S \rangle_{\text{res}}}{d\langle N \rangle_{\text{res}}} = \frac{d\langle S \rangle_{\text{res}}}{d\langle N \rangle}
\end{align*}
\]

Adding the internal dissipation term to the evaluation of the state causes the system trajectories to curve as seen in Figure 7.38. The amount of curvature is dependent on the relative strengths of the RMPI and internal dissipation terms which correspond to the ratios of the time constants \( \tau_M \) and \( \tau_D \), respectively. As the system follows the curved trajectory, the orientation of the mass interaction operator is no longer constant, but is continuously reoriented toward the final mutual stable equilibrium point. In the case where the mass flow across the system boundary is very small, as when \( \tau_M \) approaches infinity, the internal dissipation term dominates. The resulting trajectory follows a linear path in the direction of increasing entropy with energy and mass for the system remaining constant.

Figures 7.39 to 7.41 show the results from various viewpoints for a particular case when the IQT equation of motion includes both the RPMI and internal dissipation terms. The colored areas represent the stable equilibrium surface. The blue curve is the projection of the stable equilibrium manifold onto the \( \langle E \rangle - \langle S \rangle \) plane and is included for reference. The cusp-like feature seen in Figure 7.42 is an artifact of the symmetries inherent in the data set that was used to calculate the equilibrium surface. In actuality, the equilibrium surface extends all the way to the energy axis.

The evolution of the state operator for the system is shown in Figure 7.42. The figure illustrates that the IQT equation of motion can be extended to predict the rearrangement of energy among the system energy eigenlevels for an open system undergoing a mass interaction and internal dissipation.
Figure 7.42. The evolution of the state matrix probabilities for the simple open system evolving according to the IQT equation of motion with internal dissipation and RPMI terms for Figures 7.39 to 7.41.

Figure 7.43. Internal energy as function of time for the system of Figures 7.39 to 7.41.
Figures 7.43 to 7.45 show the related changes of energy, particle number and entropy as functions of time. It is seen that the change in energy is closely correlated with the change in particle number. Indeed, a mass interaction requires that energy and mass flow in the same direction across the system boundary.
IQT is a theory that not only assumes that entropy exists at quantum mechanical scales but also asserts that entropy and irreversibility have their origin in QM and the properties of matter that Quantum Mechanics describes. In so doing, IQT remains at all times fully consistent with the Second Law while other more widely used methodologies such as QSM and QT do not. It is evident from the IQT literature as well as the results from the current work that IQT is a rational, well thought out theory that is worthy of further study and ultimately of the careful scrutiny that only experiments can provide. Ideally, progress should continue on the two fronts of the extension of the theory and rigorous testing by a variety of experiments.

The results of the research presented herein indicate that the goals for the two major original contributions outlined in Chapter 1 of both practical and theoretical interest have been achieved. On the practical side, the discussions and results herein show that the evolution of hydrogen storage on a carbon nanotube, starting far from stable equilibrium, can be successfully modeled using IQT in 3D. From the standpoint of theory, it has been successfully shown how IQT can be extended to phenomenologically model heat and mass interactions using a rotational transform of the IQT dissipation operator. For the mass interaction case, the RPMI operator had not existed prior to this work and is, thus, an original contribution to IQT. In addition, important original work has been put forward in presenting comparisons of the IQT models with the data from experiments found in the literature. What follows is a short discussion of some of the conclusions that can be made due to work done herein, questions which will hopefully prompt further enquiry, and suggestions for future work.

8.1 Validation of the H$_2$-Nanotube Storage Model

IQT has been applied successfully here to modeling the 3D thermodynamic evolution of a nanoscale system of hydrogen molecules in a tank that contains a carbon nanotube. The thermodynamic description in time which results provides the exact and unique path taken by the
system in relaxing from some initial state far from stable equilibrium to a final state of stable equilibrium. Most of the principal challenges of implementing the model have been addressed if not completely overcome. The pertinent issues include the specification and construction of the carbon nanotube structure with realistic Lennard-Jones interaction potentials between the carbon and hydrogen, the solving of the two-particle energy eigenvalue problem for carbon-hydrogen and hydrogen-hydrogen interactions with respect to the nanotube using Finite Element techniques. Additional progress includes the creation of a realistic if approximate procedure for constructing system energy eigenlevels for multiple pairs of hydrogen molecules and the development of coarse-graining and scaling procedures to allow the system to be accurately modeled with a small representative subset of system energy eigenlevels in lieu of dealing with a myriad and unmanageable number of levels for an actual system. The results of the IQT model for hydrogen storage has been shown to compare well, at least in a qualitative sense, with the results obtained by GCMC and MD models at stable equilibrium. The improvement of our model to three dimensions holds the prospect of being able to make future comparisons to other well-accepted simulation methods as well as experimental data. Such comparisons cannot help but be useful in making improvements to the present IQT hydrogen storage model as well as testing IQT predictions with real world results.

The current standard for dynamic modeling at a microscopic scale is the technique of MD. MC methods and current experiments can produce results that at present are largely useful for confirming behavior at stable equilibrium. MD, however, can readily model systems that are far from equilibrium. If a strong effort at validation of the H₂-nanotube model using IQT is to be made, future work should focus on comparing results with MD simulations. The development of a MD simulation should be fairly straightforward and is, in fact, already the subject of current work of M. R. von Spakovsky in collaboration with G. P. Beretta and colleagues. Similar simulations of this kind are presented in the literature. Written codes may already be available. Numerous runs might have to be done to simulate a “probability cloud” that is analogous to the wave functions that are typical of IQT and QM. Effort may have to be expended to create in the IQT model a more localized initial condition for the H₂ molecules. A judicious superposition of the eigenfunctions could produce spikes of high probability within the system that represent the initial locations of the hydrogen molecules.
8.2 IQT Heat and Mass Interaction Models

The efforts to extend the IQT theory of isolated systems to systems that interact with both heat and mass reservoirs have been encouraging. There are issues, however, that require additional clarification. The generalization of steepest entropy increase to paths that vary in both energy and entropy for system evolution needs verification. The assumption that the system path follows steepest entropy increase with respect to a transformed coordinate system has worked reasonably well in terms of matching experimental data. However, the inflection points and singularities that are seen are so far unexplained. Herein the time functional $\tau$ has been assumed to be a constant. It is not evident in which cases a variable time functional $\tau(\rho)$ should be used. A $\tau$ that varies implies a changing strength of the interaction between system and reservoir that goes beyond the system seeking a steepest path toward stable equilibrium and so would require additional justification.

For the evolution of a reversible, conservative system, the equation of motion is based on the notion of “least action” as expressed by a minimal functional for the time integral of the Lagrangian of the system. For dissipative systems, descriptions based on the idea of “lowest entropy production rate” or “greatest entropy ascent”, as in this work, are asserted. Theoretically, it is not clear what the correct extremum of the path to stable equilibrium should be for cases when both energy and entropy are involved. The path of steepest entropy ascent coupled with steepest energy ascent/descent has been suggested here.

8.3 Experimental Validation of IQT

Simulations using the equation of motion of IQT are seen to correspond closely to data from two experiments that show non-equilibrium relaxations at atomistic scales. Thus, there appears to be support for the idea as proposed by IQT that dissipation due to internal irreversibilities occur for systems even at these small scales, i.e., that there is no “irreversibility paradox”. The findings, though not conclusive, nonetheless warrant the development of additional experiments. Further tests need to be specifically designed to verify the claims of IQT that the entropy is indeed a fundamental property of matter in the same way that inertial mass, energy, and momentum are. The results herein suggest several possible experiments.
It would be useful for Rb spin relaxation experiments similar to Kukolich (1968) and Nagel and Haworth (1966) to be rerun in a more careful fashion to determine whether the S-shaped decay curve with its stair-step feature predicted by IQT can be duplicated in a single experiment. To preserve both frequency components of the transmitted signal, the probe beam should be on resonance but weak enough so as to keep any re-pumping effects by the probe beam negligible. Variations of the experiment using differing pressures, vessel coatings and external magnetic fields, etc. might be effective in distinguishing the damping of the signal due to Rb collisions and field effects from that of internal relaxation.

A possible variation of the Turchette et al. (2000) experiment, which could test for the presence of internal dissipation, is to employ an interaction time with the reservoir that is much shorter than the measurement interval. The interaction would serve as a perturbation after which the system would be allowed to evolve on its own. The system could then be examined to see whether the evolution is consistent with the expected magnitude of internal dissipation. Of course, care must be taken to differentiate the results from the effects of the $1/f$ noise emitted by the electrodes and of ambient vacuum noise, which is relatively weaker but is said to always be present.

Another experiment to verify the existence of spontaneous internal dissipation would be to vary the strength of the reservoir to see whether the resulting trajectories of the state of the system in the $\langle E \rangle - \langle S \rangle$ plane vary in curvature as IQT predicts. The reservoir temperature would remain constant. Spontaneous relaxation should cause curvature of the path in the direction of increasing entropy. The stronger heat interactions should produce straighter trajectories along the path to stable equilibrium. If curvature can be consistently measured, the ratios of the time constants of heat interaction and internal dissipation could be determined and perhaps their absolute magnitudes as well. The measurement time interval, which is a constant 3 $\mu$s in the Turchette et al. (2000), would however, need to be varied over a range of values. Perhaps the ideal reservoir temperature would be such that the state of mutual stable equilibrium is directly below the initial the state of the system in the $\langle E \rangle - \langle S \rangle$ plane. A strong argument could be made that any deviation from a vertical trajectory is due to something other than the influence of the reservoir.
It may be possible to use trapped ions to detect partial equilibrium states that IQT predicts should exist. The temperature of the external reservoir could be adjusted to produce a horizontal $\langle E \rangle - \langle S \rangle$ trajectory. The preparation of the state is then to be modified so that the state trajectory passes closely by a predicted partial equilibrium state. The presence of a partial equilibrium state could be detected by the observation of “plateaus” or flat regions (e.g., Beretta, 2006a) in the evolution curves of the state operator.

Still another experiment involving a trapped ion would be to use relatively weak reservoirs to study whether the signature of a gradual initial relaxation evolution can be detected. An initial shape of the relaxation curve that tends to be concave down would support the notion of a gradual increase in energy spreading among the energy eigenlevels of the system as is seen in IQT simulations.

Finally, another comparison between Turchette et al. (2000) and IQT can be made without the need for an experiment. One of the main points of Turchette et al. (2000) is the experimental demonstration that the lifetime of a superposition state is inversely proportion to the square of the spread in energy for the state. An IQT model for testing relaxation time as a function of the energy spread could readily be implemented to see whether the IQT results are in accordance with the experimental findings.
References


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