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Chapter One

Introduction

1.1 An Overview of Classical Thermodynamics

Energy is a concept that underlies our understanding of all physical phenomena and is a measure of the ability of a dynamical system to produce changes (motion) in its own system state as well as changes in the system states of its surroundings. Thermodynamics is a physical branch of science that deals with laws governing energy flow from one body to another and energy transformations from one form to another. These energy flow laws are captured by the fundamental principles known as the first and second laws of thermodynamics. The first law of thermodynamics gives a precise formulation of the equivalence between *heat* (i.e., the transferring of energy via temperature gradients) and *work* (i.e., the transferring of energy into coherent motion) and states that, among all system transformations, the net system energy is conserved. Hence, energy cannot be created out of nothing and cannot be destroyed; it can merely be transferred from one form to another.

The law of conservation of energy is not a mathematical truth, but rather the consequence of an immeasurable culmination of observations over the chronicle of our civilization and is a fundamental *axiom* of the science of heat. The first law does not tell us whether any particular process can actually occur, that is, it does not restrict the ability to convert work into heat or heat into work, except that energy must be conserved in the process. The second law of thermodynamics asserts that while the system energy is always conserved, it will be degraded to a point where it cannot produce any useful work. More specifically, for any cyclic process that is shielded from heat exchange with its environment, it is impossible to extract work from heat without at the same time discarding some heat, giving rise to an increasing quantity known as *entropy*.

While energy describes the state of a dynamical system, entropy is a measure of the quality of that energy reflecting changes in the status quo of the system and is associated with disorder and the amount of wasted energy in a dynamical (energy) transformation from one state (form) to another. Since the system entropy increases, the entropy of a dynamical system tends to a maximum, and thus time, as determined by system entropy increase [299, 392, 476], flows in one direction only. Even though entropy is a physical property of matter that is not directly observable, it permeates the whole of nature, regulating the *arrow of time*, and is responsible for the enfeeblement and eventual demise of the universe.[1,2] While the laws of thermodynamics form the foundation to basic engineering systems, chemical reaction systems, nuclear reactions, cosmology, and our expanding universe, many mathematicians and scientists have expressed concerns about the completeness and clarity of the different expositions of thermodynamics over its long and tortuous history; see [69, 79, 96, 172, 184, 342, 440, 447, 455].

Since the specific motion of every molecule of a thermodynamic system is impossible to predict, a *macroscopic* model of the system is typically used, with appropriate macroscopic states that include pressure, volume, temperature, internal energy, and entropy, among others. One of the key criticisms of the macroscopic viewpoint of thermodynamics, known as *classical thermodynamics*, is the inability of the model to provide enough detail of how the system really evolves; that is, it is lacking a kinetic mechanism for describing the behavior of heat and work energy.

In developing a kinetic model for heat and dynamical energy, a thermodynamically consistent energy flow model should ensure that the system energy can be modeled by a diffusion equation in the form of a *parabolic* partial differential equation or a divergence structure *first-order hyperbolic* partial differential equation arising in models involving *conservation laws*. Such systems are infinite-dimensional, and hence, finite-dimensional approximations are of very high order, giving rise to large-scale dynamical systems with macroscopic energy transfer dynamics. Since energy is a fundamental concept in the analysis of large-scale dynamical systems, and heat (energy in transition) is a fundamental concept of thermodynamics involving the capacity of hot bodies (more energetic subsystems) to produce work, thermodynamics is a theory of large-scale dynamical systems.

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[1] Many natural philosophers have associated this ravaging irrecoverability in connection to the second law of thermodynamics with an eschatological terminus of the universe. Namely, the creation of a certain degree of life and order in the universe is inevitably coupled with an even greater degree of death and disorder. A convincing proof of this bold claim has, however, never been given.

[2] The earliest perception of irreversibility of nature and the universe along with time's arrow was postulated by the ancient Greek philosopher Herakleitos ($\sim$ 535–$\sim$ 475 B.C.). Herakleitos' profound statements, *Everything is in a state of flux and nothing is stationary* and *Man cannot step into the same river twice, because neither the man nor the river is the same*, created the foundation for all other speculation on metaphysics and physics. The idea that the universe is in constant change and that there is an underlying order to this change—the *Logos*—postulates the very existence of entropy as a physical property of matter permeating all of nature and the universe.

High-dimensional dynamical systems can arise from both macroscopic and *microscopic* points of view. Microscopic thermodynamic models can have the form of a distributed-parameter model or a large-scale system model comprised of a large number of interconnected Hamiltonian subsystems. For example, in a crystalline solid every molecule in a lattice can be viewed as an undamped vibrational mode comprising a distributed-parameter model in the form of a *second-order hyperbolic* partial differential equation. In contrast to macroscopic models involving the evolution of global quantities (e.g., energy, temperature, entropy), microscopic models are based upon the modeling of local quantities that describe the atoms and molecules that make up the system and their speeds, energies, masses, angular momenta, behavior during collisions, etc. The mathematical formulations based on these quantities form the basis of *statistical mechanics*.

Thermodynamics based on statistical mechanics is known as *statistical thermodynamics* and involves the mechanics of an ensemble of many particles (atoms or molecules) wherein the detailed description of the system state loses importance and only average properties of large numbers of particles are considered. Since microscopic details are obscured on the macroscopic level, it is appropriate to view a macroscopic model as an inherent model of uncertainty. However, for a thermodynamic system the macroscopic and microscopic quantities are related since they are simply different ways of describing the same phenomena. Thus, if the global macroscopic quantities can be expressed in terms of the local microscopic quantities, then the laws of thermodynamics could be described in the language of statistical mechanics.

This interweaving of the microscopic and macroscopic points of view leads to diffusion being a natural consequence of dimensionality and, hence, uncertainty on the microscopic level, despite the fact that there is no uncertainty about the diffusion process per se. Thus, even though as a limiting case a hyperbolic partial differential equation purports to model an infinite number of modes, in reality much of the modal information (e.g., position, velocity, energies) is only poorly known, and hence, such models are largely idealizations. With increased dimensionality comes an increase in uncertainty leading to a greater reliance on macroscopic quantities so that the system model becomes more diffusive in character.

Thermodynamics was spawned from the desire to design and build efficient heat engines, and it quickly spread to speculations about the universe upon the discovery of entropy as a fundamental physical property of matter. The theory of classical thermodynamics was predominantly developed by Carnot, Clausius, Kelvin, Planck, Gibbs, and Carathéodory,[3]

[3]The theory of classical thermodynamics has also been developed over the last one and a half centuries by many other researchers. Notable contributions include the work of Maxwell, Rankine,

and its laws have become one of the most firmly established scientific achievements ever accomplished. The pioneering work of Carnot [80] was the first to establish the impossibility of a *perpetuum mobile* of the second kind[4] by constructing a cyclical process (now known as the Carnot cycle) involving four thermodynamically reversible processes operating between two heat reservoirs at different temperatures, and showing that it is impossible to extract work from heat without at the same time discarding some heat.

Carnot's main assumption (now known as Carnot's principle) was that it is impossible to perform an arbitrarily often repeatable cycle whose only effect is to produce an unlimited amount of positive work. In particular, Carnot showed that the *efficiency* of a reversible cycle[5]—that is, the ratio of the total work produced during the cycle and the amount of heat transferred from a boiler (furnace) to a cooler (refrigerator)—is bounded by a universal maximum, and this maximum is a function only of the temperatures of the boiler and the cooler, and not of the nature of the working substance.

Both heat reservoirs (i.e., furnace and refrigerator) are assumed to have an infinite source of heat so that their state is unchanged by their heat exchange with the engine (i.e., the device that performs the cycle), and hence, the engine is capable of repeating the cycle arbitrarily often. Carnot's result (now known as Carnot's theorem) was remarkably arrived at using the erroneous concept that heat is an indestructible substance, that is, the *caloric theory of heat*.[6] This theory of heat was proposed by Lavoisier and influenced by experiments due to Black involving thermal properties of materials. The theory was based on the incorrect assertion that the temperature of a body was determined by the amount of *caloric* that it contained: an imponderable, indestructible, and highly elastic fluid that surrounded all matter and whose self-repulsive nature was responsible for thermal expansion.

Different notions of the conservation of energy can be traced back to the ancient Greek philosophers Thales ($\sim$ 624–$\sim$ 546 B.C.), Herakleitos ($\sim$ 535–$\sim$ 475 B.C.), and Empedocles ($\sim$ 490–$\sim$ 430 B.C.). Herakleitos postulates

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Reech, Clapeyron, Bridgman, Kestin, Meixner, and Giles.

[4]A *perpetuum mobile* of the second kind is a cyclic device that would continuously extract heat from the environment and completely convert it into mechanical work. Since such a machine would not create energy, it would not violate the first law of thermodynamics. In contrast, a machine that creates its own energy and thus violates the first law is called a *perpetuum mobile* of the first kind.

[5]Carnot never used the terms *reversible* and *irreversible* cycles, but rather cycles that are performed in an inverse direction and order [319, p. 11]. The term *reversible* was first introduced by Kelvin [437] wherein the cycle can be run backwards.

[6]After Carnot's death, several articles were discovered wherein he had expressed doubt about the caloric theory of heat (i.e., the conservation of heat). However, these articles were not published until the late 1870s, and as such, did not influence Clausius in rejecting the caloric theory of heat and deriving Carnot's results using the energy equivalence principle of Mayer and Joule.

that nothing in nature can be created out of nothing, and nothing that disappears ceases to exist,[7] whereas Empedocles asserts that nothing comes to be or perishes in nature.[8] The mechanical equivalence principle of heat and work energy in its modern form, however, was developed by many scientists in the nineteenth century. Notable contributions include the work of Mayer, Joule, Thomson (Lord Kelvin), Thompson (Count Rumford), Helmholtz, Clausius, Maxwell, and Planck.

Even though many scientists are credited with the law of conservation of energy, it was first discovered independently by Mayer and Joule. Mayer—a surgeon—was the first to state the mechanical equivalence of heat and work energy in its modern form after noticing that his patients' blood in the tropics was a deeper red, leading him to deduce that they were consuming less oxygen, and hence less energy, in order to maintain their body temperature in a hotter climate. This observation in slower human metabolism along with the link between the body's heat release and the chemical energy released by the combustion of oxygen led Mayer to the discovery that heat and mechanical work are interchangeable.

Joule was the first to provide a series of decisive, quantitative studies in the 1840s showing the equivalence between heat and mechanical work. Specifically, he showed that if a thermally isolated system is driven from an initial state to a final state, then the work done is only a function of the initial and final equilibrium states, and is not dependent on the intermediate states or the mechanism doing the work. This path independence property along with the irrelevancy of the method by which the work was done led to the definition of the internal energy function as a new thermodynamic coordinate characterizing the quantity of energy or state of a thermodynamic system. In other words, heat or work do not contribute separately to the internal energy function; only the sum of the two matters.

Using a macroscopic approach and building on the work of Carnot, Clausius [87–90] was the first to introduce the notion of entropy as a physical property of matter and establish the two main laws of thermodynamics involving conservation of energy and nonconservation of entropy.[9] Specifically, using conservation of energy principles, Clausius showed that Carnot's principle is valid. Furthermore, Clausius postulated that it is impossible to

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[7] Μὲν οὖν φησιν εἶναι τὸ πᾶν διαιρετὸν ἀδιαίρετον, γενητὸν ἀγένητον, θνητὸν ἀθάνατον, λὸγον αἰῶνα, πατέρα υἱὸν, …ἐστίν ἕν πάντα εἶναι.

[8] Φύσις ουδενός εστίν εόντων αλλά μόνον μίξις τε, διάλλαξίς τε μιγέντων εστί, φύσις δ' επί τοις ονομάζεται ανθρώποισιν—There is no genesis with regard to any of the things in nature but rather a blending and alteration of the mixed elements; man, however, uses the word *nature* to name these events.

[9] Clausius succinctly expressed the first and second laws of thermodynamics as: "Die energie der Welt ist konstant und die entropie der Welt strebt einem maximum zu." Namely, the energy of the Universe is constant and the entropy of the Universe tends to a maximum.

perform a cyclic system transformation whose only effect is to transfer heat from a body at a given temperature to a body at a higher temperature. From this postulate Clausius established the second law of thermodynamics as a statement about entropy increase for *adiabatically isolated systems* (i.e., systems with no heat exchange with the environment).

From this statement Clausius goes on to state what have become known as the most controversial words in the history of thermodynamics and perhaps all of science; namely, the entropy of the universe is tending to a maximum, and the total state of the universe will inevitably approach a limiting state. Clausius' second law decrees that the usable energy in the universe is locked toward a path of degeneration, sliding toward a state of quietus. The fact that the entropy of the universe is a thermodynamically undefined concept led to serious criticism of Clausius' grand universal generalizations by many of his contemporaries as well as numerous scientists, natural philosophers, and theologians who followed.

Clausius' concept of the universe approaching a limiting state was inadvertently based on an analogy between a universe and a finite adiabatically isolated system possessing a finite energy content. His eschatological conclusions are far from obvious for complex dynamical systems with dynamical states far from equilibrium and involving processes beyond a simple exchange of heat and mechanical work. It is not clear where the heat absorbed by the system, if that system is the universe, needed to define the change in entropy between two system states comes from. Nor is it clear whether an infinite and endlessly expanding universe governed by the theory of general relativity has a final equilibrium state.

An additional caveat is the delineation of energy conservation when changes in the curvature of spacetime need to be accounted for. In this case, the energy density tensor in Einstein's field equations is only covariantly conserved (i.e., locally conserved in free-falling coordinates) since it does not account for gravitational energy—an unsolved problem in the general theory of relativity. In particular, conservation of energy and momentum laws, wherein a global time coordinate does not exist, has led to one of the fundamental problems in general relativity. Specifically, in general relativity involving a curved spacetime (i.e., a semi-Riemannian spacetime), the action of the gravitational field is invariant with respect to arbitrary coordinate transformations in semi-Riemannian spacetime with a nonvanishing Jacobian containing a large number of Lie groups.

In this case, it follows from Nöether's theorem [341],[10] which derives

[10] Many conservation laws are a special case of Nöether's theorem, which states that for every one-parameter group of diffeomorphisms defined on an abstract geometrical space (e.g.,

conserved quantities from symmetries and states that every differentiable symmetry of a dynamical action has a corresponding conservation law, that a large number of conservation laws exist, some of which are not physical. In contrast, the classical conservation laws of physics, which follow from time translation invariance, are determined by an invariant property under a particular Lie group with the conserved quantities corresponding to the parameters of the group. And in special relativity, conservation of energy and momentum is a consequence of invariance through the action of infinitesimal translation of the inertial coordinates, wherein the Lorentz transformation relates inertial systems in different inertial coordinates.

In general relativity, the momentum-energy equivalence principle holds only in a local region of spacetime—a flat or Minkowski spacetime. In other words, the energy-momentum conservation laws in gravitation theory involve gauge conservation laws with local time transformations, wherein the covariant transformation generators are canonical horizontal prolongations of vector fields on a world manifold,[11] and hence, in a curved spacetime there does not exist a global energy-momentum conservation law. Nevertheless, the law of conservation of energy is as close to an absolute truth as our incomprehensible universe will allow us to deduce. In his later work [89], Clausius remitted his famous claim that the entropy of the universe is tending to a maximum.

In parallel research Kelvin [240, 438] developed similar, and in some cases identical, results as Clausius, with the main difference being the absence of the concept of entropy. Kelvin's main view of thermodynamics was that of a universal irreversibility of physical phenomena occurring in nature. Kelvin further postulated that it is impossible to perform a cyclic system transformation whose only effect is to transform into work heat from a source that is at the same temperature throughout.[12] Without any supporting mathematical arguments, Kelvin goes on to state that the universe is heading toward a state of eternal rest wherein all life on Earth in

configuration manifolds, Minkowski space, Riemannian space) of a Hamiltonian dynamical system that preserves a Hamiltonian function, there exist first integrals of motion. In other words, the algebra of the group is the set of all Hamiltonian systems whose Hamiltonian functions are the first integrals of motion of the original Hamiltonian system.

[11] A world manifold is a four-dimensional orientable, noncompact, parallelizable manifold that admits a semi-Riemannian metric and a spin structure. Gravitation theories are formulated on tensor bundles that admit canonical horizontal prolongations on a vector field defined on a world manifold. These prolongations are generators of covariant transformations whose vector field components play the role of gauge parameters. Hence, in general relativity the energy-momentum flow collapses to a superpotential of a world vector field defined on a world manifold admitting gauge parameters.

[12] In the case of thermodynamic systems with positive absolute temperatures, Kelvin's postulate can be shown to be equivalent to Clausius' postulate. However, many textbooks erroneously show this equivalence without the assumption of *positive* absolute temperatures. Physical systems possessing a small number of energy levels (i.e., an inverted Boltzmann energy distribution) with negative absolute temperatures are discussed in [121, 260, 264, 307, 373].

the distant future shall perish. This claim by Kelvin involving a universal tendency toward dissipation has come to be known as the *heat death of the universe.*

The universal tendency toward dissipation and the heat death of the universe were expressed long before Kelvin by the ancient Greek philosophers Herakleitos and Leukippos (∼480–∼420 B.C.). In particular, Herakleitos states that this universe, which is the same everywhere, and which no one god or man has made, existed, exists, and will continue to exist as an eternal source of energy set on fire by its own natural laws, and will dissipate under its own laws.[13] Herakleitos' profound statement created the foundation for all metaphysics and physics and marks the beginning of science postulating the big bang theory as the origin of the universe as well as the heat death of the universe. A century after Herakleitos, Leukippos declared that from its genesis, the cosmos has spawned multitudinous worlds that evolve in accordance to a supreme law that is responsible for their expansion, enfeeblement, and eventual demise.[14]

Building on the work of Clausius and Kelvin, Planck [358, 362] refined the formulation of classical thermodynamics. From 1897 to 1964, Planck's treatise [358] underwent eleven editions and is considered the definitive exposition on classical thermodynamics. Nevertheless, these editions have several inconsistencies regarding key notions and definitions of reversible and irreversible processes.[15] Planck's main theme of thermodynamics is that entropy increase is a necessary and sufficient condition for irreversibility. Without any proof (mathematical or otherwise), he goes on to conclude that every dynamical system in nature evolves in such a way that the total entropy of all of its parts increases. In the case of reversible processes, he concludes that the total entropy remains constant.

Unlike Clausius' entropy increase conclusion, Planck's increase entropy principle is not restricted to adiabatically isolated dynamical systems. Rather, it applies to all system transformations wherein the initial states of any exogenous system, belonging to the environment and coupled to the transformed dynamical system, return to their initial condition. It is important to note that Planck's entire formulation is restricted to homogeneous systems for which the thermodynamical state is characterized by *two* thermodynamic state variables, that is, a fluid. His formulation of entropy and the second law is not defined for more complex systems that

[13] Κόσμον (τόνδε), τὸν αὐτὸν ἁπάντων, οὔτε τις θεῶν, οὔτε ἀνθρώπων ἐποίησεν, ἀλλ' ἦν ἀεὶ καὶ ἔστιν καὶ ἔσται πῦρ ἀείζωον, ἁπτόμενον μέτρα καὶ ἀποσβεννύμενον μέτρα.

[14] Είναι τε ώσπερ γενέσεις κόσμου, ούτω καί αυξήσεις καί φθίσεις καί φθοράς, κατά τινά ανάγκην.

[15] Truesdell [445, p. 328] characterizes the work as a "gloomy murk," whereas Khinchin [245, p. 142] declares it an "aggregate of logical and mathematical errors superimposed on a general confusion in the definition of the basic quantities."

are not in equilibrium and in an environment that is more complex than one comprising a system of ideal gases.

Unlike the work of Clausius, Kelvin, and Planck involving cyclical system transformations, the work of Gibbs [163] involves system equilibrium states. Specifically, Gibbs assumes a thermodynamic state of a system involving pressure, volume, temperature, energy, and entropy, among others, and proposes that an *isolated system*[16] (i.e., a system with no energy exchange with the environment) is in equilibrium if and only if in all possible variations of the state of the system that do not alter its energy, the variation of the system entropy is negative semidefinite. Thus, the system entropy is maximized at the system equilibrium.

Gibbs also proposed a complementary formulation of his *maximum entropy* principle involving a principle of *minimal energy*. Namely, for an equilibrium of any isolated system, it is necessary and sufficient that in all possible variations of the state of the system that do not alter its entropy, the variation of its energy shall either vanish or be positive. Hence, the system energy is minimized at the system equilibrium.

Gibbs' principles give necessary and sufficient conditions for a thermodynamically stable equilibrium and should be viewed as variational principles defining admissible (i.e., stable) equilibrium states. Thus, they do not provide any information about the dynamical state of the system as a function of time nor any conclusions regarding entropy increase or energy decrease in a dynamical system transformation.

Carathéodory [76, 77] was the first to give a rigorous axiomatic mathematical framework for thermodynamics. In particular, using an *equilibrium* thermodynamic theory, Carathéodory assumes a state space endowed with a Euclidean topology and defines the equilibrium state of the system using thermal and deformation coordinates. Next, he defines an *adiabatic accessibility* relation wherein a reachability condition of an adiabatic process[17] is used such that an empirical statement of the second law characterizes a mathematical structure for an abstract state space. Even though the topology in Carathéodory's thermodynamic framework is induced on $\mathbb{R}^n$ (the space of n-tuples of reals) by taking the metric to be the Euclidean distance function and constructing the corresponding neighborhoods, the metrical properties of the state space do not play a role in his theory as there is no preference for a particular set of system coordinates.

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[16] Gibbs' principle is weaker than Clausius' principle leading to the second law involving entropy increase since it holds for the more restrictive case of isolated systems.

[17] Carathéodory's definition of an adiabatic process is nonstandard and involves transformations that take place while the system remains in an *adiabatic container*; this allowed him to avoid introducing heat as a primitive variable (i.e., axiomatic element). For details see [76, 77].

Carathéodory's postulate for the second law states that in every open neighborhood of any equilibrium state of a system, there exist equilibrium states such that for some second open neighborhood contained in the first neighborhood, all the equilibrium states in the second neighborhood cannot be reached by adiabatic processes from equilibrium states in the first neighborhood. From this postulate Carathéodory goes on to show that for a special class of systems, which he called *simple systems*, there exists a *locally* defined entropy and an absolute temperature on the state space for every simple system *equilibrium state*. In other words, Carathéodory's postulate establishes the existence of an integrating factor for the heat transfer in an infinitesimal reversible process for a thermodynamic system of an arbitrary number of degrees of freedom that makes entropy an exact (i.e., total) differential.

Unlike the work of Clausius, Kelvin, Planck, and Gibbs, Carathéodory provides a topological formalism for the theory of thermodynamics, which elevates the subject to the level of other theories of modern physics. Specifically, the empirical statement of the second law is replaced by an abstract state space formalism, wherein the second law is converted into a local topological property endowed with a Euclidean metric. This parallels the development of relativity theory, wherein Einstein's original special theory started from empirical principles—e.g., the velocity of light in free space is invariant in all inertial frames—and then was replaced by an abstract geometrical structure: the Minkowski spacetime, wherein the empirical principles are converted into local topological properties of the Minkowski metric. However, one of the key limitations of Carathéodory's work is that his principle is too weak in establishing the existence of a *global* entropy function.

Adopting a microscopic viewpoint, Boltzmann [58] was the first to give a probabilistic interpretation of entropy involving different configurations of molecular motion of the microscopic dynamics. Specifically, Boltzmann reinterpreted thermodynamics in terms of molecules and atoms by relating the *mechanical* behavior of individual atoms with their *thermodynamic* behavior by suitably averaging properties of the individual atoms. In particular, even though individually each molecule and atom obeys Newtonian mechanics, he used the science of statistical mechanics to bridge between the microscopic details and the macroscopic behavior to try to find a mechanical underpinning of the second law.

Even though Boltzmann was the first to give a probabilistic interpretation of entropy as a measure of the disorder of a physical system involving the evolution toward the largest number of possible configurations of the system's states relative to its ordered initial state, Maxwell was the first to use statistical methods to understand the behavior of the kinetic theory of gases. In particular, he postulated that it is not necessary to track the positions and velocities of each individual atom and molecule, but rather it suffices to know their position and velocity distributions; concluding that the second law is merely statistical. His distribution law for the kinetic theory of gases describes an exponential function giving the statistical distribution of the velocities and energies of the gas molecules at thermal equilibrium and provides an agreement with classical (i.e., nonquantum) mechanics.

Although the Maxwell speed distribution law agrees remarkably well with observations for an assembly of weakly interacting particles that are distinguishable, it fails for indistinguishable (i.e., identical) particles at high densities. In these regions, speed distributions predicated on the principles of quantum physics must be used; namely, the Fermi-Dirac and Bose-Einstein distributions. In this case, the Maxwell statistics closely agree with the Bose-Einstein statistics for bosons (photons, α-particles, and all nuclei with an even mass number) and the Fermi-Dirac statistics for fermions (electrons, protons, and neutrons).

Boltzmann, however, further showed that even though individual atoms are assumed to obey the laws of Newtonian mechanics, by suitably averaging over the velocity distributions of these atoms the microscopic (mechanical) behavior of atoms and molecules produced effects visible on a macroscopic (thermodynamic) scale. He goes on to argue that Clausius' thermodynamic entropy (a macroscopic quantity) is proportional to the logarithm of the probability that a system will exist in the state it is in relative to all possible states it could be in. Thus, the entropy of a thermodynamic system state (macrostate) corresponds to the degree of uncertainty about the actual system mechanical state (microstate) when only the thermodynamic system state (macrostate) is known. Hence, the essence of Boltzmann thermodynamics is that thermodynamic systems with a constant energy level will evolve from a less probable state to a more probable state with the equilibrium system state corresponding to a state of maximum entropy (i.e., highest probability).

Interestingly, Boltzmann's original thinking on the subject of entropy increase involved nondecreasing of entropy as an absolute certainty and not just as a statistical certainty. In the 1870s and 1880s, his thoughts on this matter underwent significant refinements and shifted to a probabilistic viewpoint after interactions with Maxwell, Kelvin, Loschmidt, Gibbs, Poincaré, Burbury, and Zermelo; all of whom criticized his original formulation.

In statistical thermodynamics the Boltzmann entropy formula relates the entropy $\mathcal{S}$ of an ideal gas to the number of distinct microstates

$\mathcal{W}$ corresponding to a given macrostate as $\mathcal{S} = k \log_e \mathcal{W}$, where k is the Boltzmann constant.[18] Thus, the Boltzmann entropy gives the number of different microscopic configurations of a system's states that leave its macroscopic appearance unchanged, and hence, it connects the Clausius entropy, a macroscopic thermodynamic quantity, to probability, a microscopic statistical quantity.

Even though Boltzmann was the first to link the thermodynamic entropy of a macrostate for some probability distribution of all possible microstates generated by different positions and momenta of various gas molecules [57], it was Planck who first stated (without proof) this entropy formula in his work on blackbody radiation [359]. In addition, Planck was also the first to introduce the precise value of the Boltzmann constant to the formula; Boltzmann merely introduced the proportional logarithmic connection between the entropy $\mathcal{S}$ of an observed macroscopic state, or degree of disorder of a system, to the thermodynamic probability of its occurrence $\mathcal{W}$, never introducing the constant k to the formula.

To further complicate matters, in his original paper [359] Planck stated the formula without derivation or clear justification; a fact that deeply troubled Albert Einstein [130]. Despite the fact that numerous physicists consider $\mathcal{S} = k \log_e \mathcal{W}$ as the second most important formula of physics—second to Einstein's $E = mc^2$—for its unquestionable success in computing the thermodynamic entropy of isolated systems, its theoretical justification remains ambiguous and vague in most statistical thermodynamics textbooks. In this regard, Khinchin [245, p. 142] writes: "All existing attempts to give a general proof of [Boltzmann's entropy formula] must be considered as an aggregate of logical and mathematical errors superimposed on a general confusion in the definition of basic quantities."

In the first half of the twentieth century, the macroscopic (classical) and microscopic (statistical) interpretations of thermodynamics underwent a long and fierce debate. To exacerbate matters, since classical thermodynamics was formulated as a physical theory and not a mathematical theory, many scientists and mathematical physicists expressed concerns about the completeness and clarity of the mathematical foundation of thermodynamics

[18] The number of distinct microstates $\mathcal{W}$ can also be regarded as the number of solutions of the Schrödinger equation for the system giving a particular energy distribution. The Schrödinger wave equation describes how a quantum state of a system evolves over time. The solution of the equation characterizes a quantum wave function whose wavelength is related to the system momentum and frequency is related to the system energy. Unlike Planck's discrete quantum transition theory of energy when light interacts with matter, Schrödinger's quantum theory stipulates that quantum transition involves vibrational changes from one form to another; and these vibrational changes are continuous in space and time. Furthermore, if the quantum wave function is known at any given point in time, then Schrödinger's equation uniquely specifies the quantum wave function at any other moment in time, making this constituent part of quantum physics fully deterministic.

[11, 69, 447]. In fact, many fundamental conclusions arrived at by classical thermodynamics can be viewed as paradoxical.

For example, in classical thermodynamics the notion of entropy (and temperature) is only defined for equilibrium states. However, the theory concludes that nonequilibrium states transition toward equilibrium states as a consequence of the law of entropy increase! Furthermore, classical thermodynamics is restricted to systems in equilibrium. The second law infers that for any transformation occurring in an isolated system, the entropy of the final state can never be less than the entropy of the initial state. In this context, the initial and final states of the system are equilibrium states. However, by definition, an equilibrium state is a system state that has the property that whenever the state of the system starts at the equilibrium state it will remain at the equilibrium state for all future time unless an exogenous input acts on the system. Hence, the entropy of the system can only increase if the system is *not* isolated!

Many aspects of classical thermodynamics are riddled with such inconsistencies, and hence it is not surprising that many formulations of thermodynamics, especially most textbook expositions, poorly amalgamate physics with rigorous mathematics. Perhaps this is best eulogized in [447, p. 6], wherein Truesdell describes the present state of the theory of thermodynamics as a "dismal swamp of obscurity." In a desperate attempt to try to make sense of the writings of de Groot, Mazur, Casimir, and Prigogine, he goes on to state that there is "something rotten in the [thermodynamic] state of the Low Countries" [447, p. 134].

Brush [69, p. 581] remarks that "anyone who has taken a course in thermodynamics is well aware, the mathematics used in proving Clausius' theorem … [has] only the most tenuous relation to that known to mathematicians." And Born [61, p. 119] admits that "I tried hard to understand the classical foundations of the two theorems, as given by Clausius and Kelvin; … but I could not find the logical and mathematical root of these marvelous results." More recently, Arnold [11, p. 163] writes that "every mathematician knows it is impossible to understand an elementary course in thermodynamics."

As we have outlined, it is clear that there have been many different presentations of classical thermodynamics with varying hypotheses and conclusions. To exacerbate matters, there are also many vaguely defined terms and functions that are central to thermodynamics, such as entropy, enthalpy, free energy, quasi-static, nearly in equilibrium, extensive variables, intensive variables, reversible, irreversible, etc. Furthermore, these functions' domain and codomain are often unspecified and their local and global existence, uniqueness, and regularity properties are unproven.

Moreover, there are no general dynamic equations of motion, no ordinary or partial differential equations, and no general theorems providing mathematical structure and characterizing classes of solutions. Rather, we are asked to believe that a certain differential can be greater than something that is not a differential defying the syllogism of differential calculus, line integrals approximating adiabatic and isothermal paths result in alternative solutions annulling the fundamental theorem of integral calculus, and we are expected to settle for descriptive and unmathematical wordplay in explaining key principles that have far-reaching consequences in engineering, science, and cosmology.

Furthermore, the careless and considerable differences in the definitions of two of the key notions of thermodynamics—namely, the notions of reversibility and irreversibility—have contributed to the widespread confusion and lack of clarity of the exposition of classical thermodynamics over the past one and a half centuries. For example, the concept of reversible processes as defined by Carnot, Clausius, Kelvin, Planck, and Carathéodory have very different meanings. In particular, Carnot never uses the term *reversible*, but rather cycles that can be run backwards. Later he added that these cycles should proceed slowly so that the system remains in equilibrium over the entire cycle. Such system transformations are commonly referred to as *quasi-static* transformations in the thermodynamic literature. Clausius defines reversible (*umkehrbar*) cyclic and noncyclic processes as slowly varying processes wherein successive states of these processes differ by infinitesimals from the equilibrium system states. Alternatively, Kelvin's notions of reversibility involve the ability of a system to completely recover its initial state from the final system state. He does not limit his definition of reversibility to cyclic processes, and hence, a cyclic process can be reversible in the sense of Kelvin but irreversible in the sense of Carnot.

Planck introduced several notions of reversibility. His main notion of reversibility is one of *complete* reversibility and involves recoverability of the original state of the dynamical system while at the same time restoring the environment to its original condition. Unlike Clausius' notion of reversibility, Kelvin's and Planck's notions of reversibility do not require the system to exactly retrace its original trajectory in reverse order. Carathéodory's notion of reversibility involves recoverability of the system state in an adiabatic process resulting in yet another definition of thermodynamic reversibility. These subtle distinctions of (ir)reversibility are often unrecognized in the thermodynamic literature. Notable exceptions to this fact include [65,448], with [448] providing an excellent exposition of the relation between irreversibility, the second law of thermodynamics, and the arrow of time.

1.2 Thermodynamics and the Arrow of Time

The arrow of time[19] and the second law of thermodynamics is one of the most famous and controversial problems in physics. The controversy between ontological time (i.e., a timeless universe) and the arrow of time (i.e., a constantly changing universe) can be traced back to the famous dialogues between the ancient Greek philosophers Parmenides[20] and Herakleitos on being and becoming. Parmenides, like Einstein, insisted that time is an illusion, that there is nothing new, and that everything is (being) and will forever be. This statement is of course paradoxical since the status quo changed after Parmenides wrote his famous poem *On Nature*.

Parmenides maintained that we all exist *within* spacetime, and time is a one-dimensional continuum in which all events, regardless of when they happen from any given perspective, simply *are*. All events exist endlessly and universally, and occupy ordered points in spacetime, and hence, reality envelops past, present, and future *equally*. More specifically, our picture of the universe at a given moment is identical and contains exactly the same events; we simply have different *conceptions* of what exists at that moment, and hence, different *conceptions* of reality. Conversely, the Heraclitean flux doctrine maintains that nothing ever is, and everything is becoming. In this regard, time gives a *different* ontological status of past, present, and future resulting in an ontological transition, creation, and actualization of events. More specifically, the unfolding of events in the flow of time have counterparts in reality.

Herakleitos' aphorism is predicated on change (becoming); namely, the universe is in a constant state of flux and nothing is stationary—Τα πάντα ρεί καί ούδέν μένει. Furthermore, Herakleitos goes on to state that the universe evolves in accordance with its own laws, which are the only unchangeable things in the universe (e.g., universal conservation and nonconservation laws). His statements that everything is in a state of flux—Τα πάντα ρεί—and that man cannot step into the same river twice, because

[19]The phrase *arrow of time* was coined by Eddington in his book *The Nature of the Physical World* [123] and connotes the one-way direction of entropy increase educed from the second law of thermodynamics. Other phrases include the *thermodynamic arrow* and the *entropic arrow of time*. Long before Eddington, however, philosophers and scientists addressed deep questions about time and its direction.

[20]Parmenides (∼515–∼450 B.C.) maintained that there is neither time nor motion. His pupil Zeno of Elea (∼490–∼430 B.C.) constructed four paradoxes—the dichotomy, the Achilles, the flying arrow, and the stadium—to prove that motion is impossible. His logic was "immeasurably subtle and profound" and even though infinitesimal calculus provides a tool that explains Zeno's paradoxes, the paradoxes stand at the intersection of reality and our perception of it; and they remain at the cutting edge of our understanding of space, time, and spacetime [316].

neither the man nor the river is the same—Ποταμείς τοίς αυτοίς εμβαίνομεν τε καί ουκ εμβαίνομεν, είμεν τε καί ουκ είμεν—give the earliest perception of irreversibility of nature and the universe along with time's arrow. The idea that the universe is in constant change and there is an underlying order to this change—the Logos (Λόγος)—postulates the existence of entropy as a physical property of matter permeating the whole of nature and the universe.

Herakleitos' statements are completely consistent with the laws of thermodynamics, which are intimately connected to the irreversibility of dynamical processes in nature. In addition, his aphorisms go beyond the worldview of classical thermodynamics and have deep relativistic ramifications to the spacetime fabric of the cosmos. Specifically, Herakleitos' profound statement—All matter is exchanged for energy, and energy for all matter (Πυρός τε ἀνταμοιβὴ τὰ πάντα καὶ πῦρ ἁπάντων)—is a statement of the law of conservation of mass-energy and is a precursor to the principle of relativity. In describing the nature of the universe Herakleitos postulates that nothing can be created out of nothing, and nothing that disappears ceases to exist. This totality of forms, or mass-energy equivalence, is eternal[21] and unchangeable in a constantly changing universe.

The arrow of time[22] remains one of physics' most perplexing enigmas [122, 178, 220, 254, 297, 362, 377, 463]. Even though time is one of the most familiar concepts mankind has ever encountered, it is the least understood. Puzzling questions of time's mysteries have remained unanswered throughout the centuries.[23] Questions such as, Where does time come from? What would our universe look like without time? Can there be more than one dimension to time? Is time truly a fundamental appurtenance woven into the fabric of the universe, or is it just a useful edifice for organizing our perception of events? Why is the concept of time hardly ever found in the most fundamental physical laws of nature and the universe? Can we go back in time? And if so, can we change past events?

Human experience perceives time flow as unidirectional; the present

[21]It is interesting to note that, despite his steadfast belief in change, Herakleitos embraced the concept of *eternity* as opposed to Parmenides' *endless duration* concept in which all events making up the universe are static and unchanging, eternally occupying fixed points in a frozen immutable future of spacetime.

[22]Perhaps a better expression here is the *geodesic arrow of time*, since, as Einstein's theory of relativity shows, time and space are intricately coupled, and hence one cannot curve space without involving time as well. Thus, time has a shape that goes along with its directionality.

[23]Plato (∼428–∼348 B.C.) writes that time was created as an image of the eternal. While time is everlasting, time is the outcome of change (motion) in the universe. And as night and day and month and the like are all part of time, without the physical universe time ceases to exist. Thus, the creation of the universe has spawned the arrow of time—Χρόνον τε γενέσθαι εἰκόνα τοῦ ἀιδίου. Κἀκεῖνον μὲν ἀεί μένειν, τὴν δὲ τοῦ οὐρανοῦ φορὰν χρόνον εἶναι· καὶ γὰρ νύκτα καὶ ἡμέραν καὶ μῆνα καὶ τὰ τοιαῦτα πάντα χρόνου μέρη εἶναι. Διόπερ ἄνευ τῆς τοῦ κόσμου φύσεως οὐκ εἶναι χρόνον· ἅμα γὰρ ὑπάρχειν αὐτῷ καὶ χρόνον εἶναι.

is forever flowing toward the future and away from a forever fixed past. Many scientists have attributed this *emergence* of the direction of time flow to the second law of thermodynamics due to its intimate connection to the irreversibility of dynamical processes.[24] In this regard, thermodynamics is disjoint from Newtonian and Hamiltonian mechanics (including Einstein's relativistic and Schrödinger's quantum extensions), since these theories are invariant under time reversal, that is, they make no distinction between one direction of time and the other. Such theories possess a *time-reversal symmetry*, wherein, from any given moment of time, the governing laws treat past and future in exactly the same way [258].[25] It is important to stress here that time-reversal symmetry applies to dynamical processes whose reversal is allowed by the physical laws of nature, *not* a reversal of time itself. It is irrelevant whether or not the reversed dynamical process actually occurs in nature; it suffices that the theory allows for the reversed process to occur.

The simplest notion of time-reversal symmetry is the statement wherein the physical theory in question is time-reversal symmetric in the sense that given any solution $x(t)$ to a set of dynamic equations describing the physical laws, then $x(-t)$ is also a solution to the dynamic equations. For example, in Newtonian mechanics this implies that there exists a transformation $\mathcal{R}(q,p)$ such that $\mathcal{R}(q,p) \circ x(t) = x(-t) \circ \mathcal{R}(q,p)$, where $\circ$ denotes the composition operator and $x(-t) = [q(-t),\ -p(-t)]^{\mathrm{T}}$ represents the particles that pass through the same position as $q(t)$, but in reverse order and with reverse velocity $-p(-t)$. It is important to note that if the physical laws describe the dynamics of particles in the presence of a field (e.g., an electromagnetic field), then the reversal of the particle velocities is insufficient for the equations to yield time-reversal symmetry. In this case, it is also necessary to reverse the field, which can be accomplished by modifying the transformation $\mathcal{R}$ accordingly.

As an example of time-reversal symmetry, a film run backwards of a harmonic oscillator over a full period or a planet orbiting the Sun would represent possible events. In contrast, a film run backwards of water in a glass coalescing into a solid ice cube or ashes self-assembling into a log of wood would immediately be identified as an impossible event.

[24]In statistical thermodynamics the arrow of time is viewed as a consequence of high system dimensionality and randomness. However, since in statistical thermodynamics it is not absolutely certain that entropy increases in every dynamical process, the direction of time, as determined by entropy increase, has only statistical certainty and not an absolute certainty. Hence, it cannot be concluded from statistical thermodynamics that time has a unique direction of flow.

[25]There is an exception to this statement involving the laws of physics describing weak nuclear force interactions in Yang-Mills quantum fields [471]. In particular, in certain experimental situations involving high-energy atomic and subatomic collisions, meson particles (K-mesons and B-mesons) exhibit time-reversal asymmetry [85]. However, under a combined transformation involving *charge conjugation* $\mathcal{C}$, which replaces the particles with their antiparticles, *parity* $\mathcal{P}$, which inverts the particles' positions through the origin, and a time-reversal *involution* $\mathcal{R}$, which replaces t with $-t$, the particles' behavior is $\mathcal{CPR}$-invariant. For details see [85].

Over the centuries, many philosophers and scientists shared the views of a Parmenidean frozen river time theory. However, since the advent of the science of thermodynamics in the nineteenth century, philosophy and science took a different point of view with the writings of Hegel, Bergson, Heidegger, Clausius, Kelvin, and Boltzmann; one involving time as our existential dimension. The idea that the second law of thermodynamics provides a physical foundation for the arrow of time has been postulated by many authors [123, 369, 377].[26] However, a convincing mathematical argument of this claim has never been given [178, 254, 448].

The complexities inherent with the afore statement are subtle and are intimately coupled with the universality of thermodynamics, entropy, gravity, and cosmology (see Section 17.4 and Chapter 18). A common misconception of the principle of the entropy increase is surmising that if entropy increases in forward time, then it necessarily decreases in backward time. However, entropy and the second law *do not* alter the (known) laws of physics in any way—the laws have no temporal orientation. In the absence of a unified dynamical systems theory of thermodynamics with Newtonian and Einsteinian mechanics, the second law is *derivative* to the physical laws of motion. Thus, since the (known) laws of nature are autonomous to temporal orientation, the second law implies, with identical certainty, that entropy increases both forward and backward in time from any given moment in time.

This statement, however, is not true in general; it is true only if the primordial state of the universe did *not* begin in a highly ordered, low entropy state. However, quantum fluctuations in Higgs boson particles[27] stretched out by inflation and inflationary cosmology followed by the big bang [183] tells us that the early universe began its trajectory in a highly ordered, low entropy state, which allows us to educe that the entropic arrow of time is *not* a *double-headed* arrow and that the future is indeed in the direction of increasing entropy. This further establishes that the concept of time flow directionality, which almost never enters in any physical theory, is a defining marvel of thermodynamics. Heat (i.e., energy in transition), like gravity, permeates every substance in the universe and its radiation spreads to every part of spacetime. However, unlike gravity, the directional

[26]Conversely, one can also find many authors who maintain that the second law of thermodynamics has nothing to do with irreversibility or the arrow of time [124, 231, 261]; these authors largely maintain that thermodynamic irreversibility and the absence of a temporal orientation of the rest of the laws of physics are disjoint notions. This is due to the fact that classical thermodynamics is riddled with many logical and mathematical inconsistencies with carelessly defined notation and terms. And more importantly, with the notable exception of [195], a dynamical systems foundation of thermodynamics is nonexistent in the literature.

[27]The Higgs boson is an elementary particle (i.e., a particle with an unknown substructure) containing matter (particle mass) and radiation (emission or transmission of energy), and is the finest quantum constituent of the Higgs field. See Chapter 17 for further details.

continuity of entropy and time (i.e., the entropic arrow of time) elevates thermodynamics to a sui generis physical theory of nature.

1.3 Modern Thermodynamics, Information Theory, and Statistical Energy Analysis

In an attempt to generalize classical thermodynamics to nonequilibrium thermodynamics, Onsager [347, 348] developed reciprocity theorems for irreversible processes based on the concept of a local equilibrium that can be described in terms of state variables that are predicated on linear approximations of thermodynamic equilibrium variables. Onsager's theorem pertains to the thermodynamics of linear systems, wherein a symmetric reciprocal relation applies between forces and fluxes. In particular, a flow or flux of matter in thermodiffusion is caused by the force exerted by the thermal gradient. Conversely, a concentration gradient causes a heat flow, an effect that has been experimentally verified for linear transport processes involving thermodiffusion, thermoelectric, and thermomagnetic effects.

Classical irreversible thermodynamics [114, 272, 477], as originally developed by Onsager, characterizes the rate of entropy production of irreversible processes as a sum of the product of fluxes with their associated forces, postulating a linear relationship between the fluxes and forces. The thermodynamic fluxes in the Onsager formulation include the effects of heat conduction, flow of matter (i.e., diffusion), mechanical dissipation (i.e., viscosity), and chemical reactions. Well-known laws of physics confirm Onsager's reciprocity relationships for near equilibrium systems. For example, Fourier's law of heat conduction asserts that heat flow is proportional to a temperature gradient and Fick's law describes a proportional relationship between diffusion and a chemical concentration gradient. Onsager's thermodynamic theory, however, is only correct for near equilibrium processes, wherein a local and linear instantaneous relation between the fluxes and forces holds.

Casimir [82] extended Onsager's principle of macroscopic reversibility to explain the relations between irreversible processes and network theory involving the coupling effects of electrical currents and resistance on entropy production. The Onsager-Casimir reciprocal relations treat only the irreversible aspects of system processes, and thus the theory is an algebraic theory that is primarily restricted to describing (time-independent) system steady states. In addition, the Onsager-Casimir formalism is restricted to linear systems, wherein a linearity restriction is placed on the admissible constitutive relations between the thermodynamic forces and fluxes. Another limitation of the Onsager-Casimir framework is the difficulty in providing a macroscopic description for large-scale complex dynamical systems. In addition, the Onsager-Casimir reciprical relations are not valid on the microscopic thermodynamic level.

Building on Onsager's classical irreversible thermodynamic theory, Prigogine [166, 367, 368] developed a thermodynamic theory of *dissipative nonequilibrium structures*. This theory involves kinetics describing the behavior of systems that are away from equilibrium states. However, Prigogine's thermodynamics lacks functions of the system state, and hence, his concept of entropy for a system away from equilibrium does not have a total differential. Furthermore, Prigogine's characterization of dissipative structures is predicated on a linear expansion of the entropy function about a particular equilibrium, and hence, is limited to the neighborhood of the equilibrium. This is a severe restriction on the applicability of this theory. In addition, his entropy cannot be calculated nor determined [165, 282]. Moreover, the theory requires that locally applied exogenous heat fluxes propagate at infinite velocities across a thermodynamic body, violating both experimental evidence and the principle of causality. To paraphrase Penrose, Prigogine's thermodynamic theory at best should be regarded as a trial or dead end.

In an attempt to extend Onsager's classical irreversible thermodynamic theory beyond a local equilibrium hypothesis, *extended irreversible thermodynamics* was developed in the literature [81, 236] wherein, in addition to the classical thermodynamic variables, dissipating fluxes are introduced as new independent variables providing a link between classical thermodynamics and flux dynamics. These complementary thermodynamic variables involve nonequilibrium quantities and take the form of dissipative fluxes and include heat, viscous pressure, matter, and electric current fluxes, among others. These fluxes are associated with microscopic operators of nonequilibrium statistical mechanics and the kinetic theory of gases, and effectively describe systems with long relaxation times (e.g., low-temperature solids, superfluids, and viscoelastic fluids).

Even though extended irreversible thermodynamics generalizes classical thermodynamics to nonequilibrium systems, the complementary variables are treated on the same level as the classical thermodynamic variables and hence lack any evolution equations. To compensate for this, additional rate equations are introduced for the dissipative fluxes. Specifically, the fluxes are selected as state variables wherein the constitutive equations of Fourier, Fick, Newton, and Ohm are replaced by first-order time evolution equations that include memory and nonlocal effects.

However, unlike the classical thermodynamic variables, which satisfy conservation of mass and energy and are compatible with the second law of thermodynamics, no specific criteria are specified for the evolution equations of the dissipative fluxes. Furthermore, since every dissipative flux is formulated as a thermodynamic variable characterized by a single evolution equation with the system entropy being a function of the fluxes, extended irreversible thermodynamic theories tend to be incompatible with classical thermodynamics. Specifically, the theory yields different definitions for temperature and entropy when specialized to equilibrium thermodynamic systems.

In the last half of the twentieth century, thermodynamics was reformulated as a global nonlinear field theory with the ultimate objective to determine the independent field variables of this theory [92, 333, 393, 446]. This aspect of thermodynamics, which became known as *rational thermodynamics*, was predicated on an entirely new axiomatic approach. As a result of this approach, modern continuum thermodynamics was developed using theories from elastic materials, viscous materials, and materials with memory [91, 106, 107, 182]. The main difference between classical thermodynamics and rational thermodynamics can be traced back to the fact that in rational thermodynamics the second law is not interpreted as a restriction on the transformations a system can undergo, but rather as a restriction on the system's constitutive equations.

Rational thermodynamics is formulated based on nonphysical interpretations of absolute temperature and entropy notions that are not limited to near equilibrium states. Moreover, the thermodynamic system has memory, and hence, the dynamic behavior of the system is determined not only by the present value of the thermodynamic state variables but also by the history of their past values. In addition, the second law of thermodynamics is expressed using the Clausius-Duhem inequality.

Rational thermodynamics is not a thermodynamic theory in the classical sense but rather a theory of thermomechanics of continuous media. This theory, which is also known as *modern continuum thermodynamics*, abandons the concept of a local equilibrium and involves general conservation laws (mass, momentum, energy) for defining a thermodynamic state of a body using a set of postulates and constitutive functionals. These postulates, which include the principles of admissibility (i.e., entropy principle), objectivity or covariance (i.e., reference frame invariance), local action (i.e., influence of a neighborhood), memory (i.e., a dynamic), and symmetry, are applied to the constitutive equations describing the thermodynamic process.

Modern continuum thermodynamics has been extended to account for nonlinear irreversible processes such as the existence of thresholds, plasticity, and hysteresis [118, 241, 309, 310]. These extensions use convex analysis, semigroup theory, and nonlinear programming theory but can lack a clear characterization of the space over which the thermodynamical state variables evolve. The principal weakness of rational thermodynamics is that its range of applicability is limited to closed systems (see Chapter 2) with a single absolute temperature. Thus, it is not applicable to condensed matter physics (e.g., diffusing mixtures or plasma). Furthermore, it does not provide a unique entropy characterization that satisfies the Clausius inequality.

More recently, a contribution to *equilibrium* thermodynamics is given in [280]. This work builds on the work of Carathéodory [76, 77] and Giles [164] by developing a thermodynamic system representation involving a state space on which an adiabatic accessibility relation is defined. The existence and uniqueness of an entropy function is established as a consequence of adiabatic accessibility among *equilibrium states*. As in Carathéodory's work, the authors in [280] also restrict their attention to simple (possibly interconnected) systems in order to arrive at an entropy increase principle. However, it should be noted that the notion of a simple system in [280] is not equivalent to that of Carathéodory's notion of a simple system.

Connections between thermodynamics and systems theory as well as information theory have also been explored in the literature [35,37,66,68,192, 353,463,464,472,478]. Information theory has deep connections to physics in general, and thermodynamics in particular. Many scientists have postulated that information is physical and have suggested that the bit is the irreducible kernel in the universe and it is more fundamental than matter itself, with information forming the very core of existence [167,259]. To produce change (motion) requires energy, whereas to direct this change requires information. In other words, energy takes different forms, but these forms are determined by information. Arguments about the nature of reality is deeply rooted in quantum information, which gives rise to every particle, every force field, and spacetime itself.

In quantum mechanics information can be inaccessible but not annihilated. In other words, information can never be destroyed despite the fact that imperfect system state distinguishability abounds in quantum physics, wherein the Heisenberg uncertainty principle brought the demise of determinism in the microcosm of science. The afore statement concerning the nonannihilation of information is not without its controversy in physics and is at the heart of the black hole information paradox, which resulted from the incomplete unification of quantum mechanics and general relativity.

Specifically, Hawking and Bekenstein [28, 208] argued that general relativity and quantum field theory were inconsistent with the principle that information cannot be lost. In particular, as a consequence of quantum fluctuations near a black hole's event horizon,[28] they showed that black holes radiate particles, and hence, slowly evaporate. And since matter falling into a black hole carries information in its structure, organization, and quantum states, black hole evaporation via radiation obliterates information.

However, using Richard Feynman's sum over histories path integral formulation of quantum theory to the topology of spacetime [146], Hawking later showed that quantum gravity is *unitary* (i.e., the sum of probabilities for all possible outcomes of a given event is unity) and that black holes are never unambiguously black. That is, black holes slowly dissipate before they ever truly form, allowing radiation to contain information, and hence, information is not lost, obviating the information paradox.

In quantum mechanics the Heisenberg uncertainty principle is a consequence of the fact that the outcome of an experiment is affected, or even determined, when observed. The Heisenberg uncertainty principle states that it is impossible to measure both the position and momentum of a particle with absolute precision at a microscopic level, and the product of the uncertainties in these measured values is in the order of the magnitude of the Planck constant. The determination of energy and time is also subject to the same uncertainty principle. The principle is not a statement about our inability to develop accurate measuring instruments, but rather a statement about an intrinsic property of nature; namely, nature has an inherent indeterminacy. And this is a consequence of the fact that any attempt at observing nature will disturb the system under observation, resulting in a lack of precision.

Quantum mechanics provides a probabilistic theory of nature, wherein the equations describe the average behavior of a large collection of identical particles and not the behavior of individual particles. Einstein maintained that the theory was incomplete albeit a good approximation in describing nature. He further asserted that when quantum mechanics had been completed, it would deal with certainties. In a letter to Max Born he states his famous "God does not play dice" dictum, writing: "The theory produces a great deal but hardly brings us closer to the secret of the Old One. I am at all events convinced that He does not play dice" [60, p. 90]. A profound ramification of the Heisenberg uncertainty principle is that the macroscopic principle of causality does not apply at the atomic level.

Information theory addresses the quantification, storage, and communication of information. The study of the effectiveness of communication

[28] In relativistic physics, an *event horizon* is a boundary delineating the set of points in spacetime beyond which events cannot affect an outside observer. In the present context, it refers to the boundary beyond which events cannot escape the black hole's gravitational field.

channels in transmitting information was pioneered by Shannon [406]. Information is encoded, stored (by codes), transmitted through channels of limited capacity, and then decoded. The effectiveness of this process is measured by the *Shannon capacity* of the channel and involves the entropy of a set of events that measure the uncertainty of this set. These channels function as input-output devices that take letters from an input alphabet and transmit letters to an output alphabet with various error probabilities that depend on noise. Hence, entropy in an information-theoretic context is a measure of information uncertainty. Simply put—information is *not* free and is linked to the cost of computing the behavior of matter and energy in our universe [39]. For an excellent exposition of these different facets of thermodynamics see [175].

Thermodynamic principles have also been repeatedly used in coupled mechanical systems to arrive at energy flow models. Specifically, in an attempt to approximate high-dimensional dynamics of large-scale structural (oscillatory) systems with a low-dimensional diffusive (nonoscillatory) dynamical model, structural dynamicists have developed thermodynamic energy flow models using stochastic energy flow techniques. In particular, statistical energy analysis (SEA) predicated on averaging system states over the statistics of the uncertain system parameters has been extensively developed for mechanical and acoustic vibration problems [78, 238, 270, 297, 414, 468]. The aim of SEA is to establish that many concepts of energy flow modeling in high-dimensional mechanical systems have clear connections with statistical mechanics of many particle systems, and hence, the second law of thermodynamics applies to large-scale coupled mechanical systems with modal energies playing the role of temperatures.

Thermodynamic models are derived from large-scale dynamical systems of discrete subsystems involving stored energy flow among subsystems based on the assumption of weak subsystem coupling or identical subsystems. However, the ability of SEA to predict the dynamic behavior of a complex large-scale dynamical system in terms of pairwise subsystem interactions is severely limited by the coupling strength of the remaining subsystems on the subsystem pair. Hence, it is not surprising that SEA energy flow predictions for large-scale systems with strong coupling can be erroneous. From the rigorous perspective of dynamical systems theory, the theoretical foundations of SEA remain inadequate since well-defined mathematical assumptions of the theory are not adequately delineated.

Alternatively, a deterministic thermodynamically motivated energy flow modeling for structural systems is addressed in [247–249]. This approach exploits energy flow models in terms of thermodynamic energy (i.e., the ability to dissipate heat) as opposed to stored energy and is not limited to weak subsystem coupling. A stochastic energy flow *compartmental model* (i.e., a model characterized by energy conservation laws) predicated on averaging system states over the statistics of stochastic system exogenous disturbances is developed in [37]. The basic result demonstrates how linear compartmental models arise from second-moment analysis of state space systems under the assumption of weak coupling. Even though these results can be potentially applicable to linear large-scale dynamical systems with weak coupling, such connections are not explored in [37]. With the notable exception of [78], and more recently [273], none of the aforementioned SEA-related works addresses the second law of thermodynamics involving entropy notions in the energy flow between subsystems.

Motivated by the manifestation of emergent behavior of macroscopic energy transfer in crystalline solids modeled as a lattice of identical molecules involving undamped vibrations, the authors in [44] analyze energy equipartition in linear Hamiltonian systems using average-preserving symmetries. Specifically, the authors consider a Lie group of phase space symmetries of a linear Hamiltonian system and characterize the subgroup of symmetries whose elements are also symmetries of every Hamiltonian system and preserve the time averages of quadratic Hamiltonian functions along system trajectories. In the very specific case of distinct natural frequencies and a two-degree-of-freedom system consisting of an interconnected pair of identical undamped oscillators, the authors show that the time-averaged oscillator energies reach an equipartitioned state. For this limited case, this result shows that time averaging leads to the emergence of damping in lossless Hamiltonian dynamical systems.

1.4 Dynamical Systems

Dynamical systems theory provides a universal mathematical formalism predicated on modern analysis and has become the prevailing language of modern science as it provides the foundation for unlocking many of the mysteries in nature and the universe that involve spatial and temporal evolution. Given that irreversible thermodynamic systems involve a definite direction of evolution, it is natural to merge the two universalisms of thermodynamics and dynamical systems under a single compendium, with the latter providing an ideal language for the former.

A *system* is a combination of components or parts that is perceived as a single entity. The parts making up the system may be clearly or vaguely defined. These parts are related to each other through a particular set of variables, called the *states* of the system, that, together with the knowledge of any system inputs, completely determine the behavior of the system at any given time. A *dynamical system* is a system whose state changes with time. Dynamical systems theory was fathered by Henri Poincaré [363–365], sturdily developed by Birkhoff [50, 51], and has evolved to become one of the most universal mathematical formalisms used to explain system manifestations of nature that involve time.

A dynamical system can be regarded as a mathematical model structure involving an input, state, and output that can capture the dynamical description of a given class of physical systems. Specifically, a *closed* dynamical system consists of three elements—namely, a setting called the *state space*, which is assumed to be Hausdorff[29] and in which the dynamical behavior takes place, such as a torus, topological space, manifold, or locally compact metric space; a mathematical rule or *dynamic*, which specifies the evolution of the system over time; and an initial condition or *state* from which the system starts at some initial time.

An *open* dynamical system interacts with the environment through system *inputs* and system *outputs* and can be viewed as a precise mathematical object that maps exogenous inputs (causes, disturbances) into outputs (effects, responses) via a set of internal variables, the state, which characterizes the influence of past inputs. For dynamical systems described by ordinary differential equations, the independent variable is time, whereas spatially distributed systems described by partial differential equations involve multiple independent variables reflecting, for example, time and space.

The state of a dynamical system can be regarded as an information storage or memory of past system events. The set of (internal) states of a dynamical system must be sufficiently rich to completely determine the behavior of the system for any future time. Hence, the state of a dynamical system at a given time is uniquely determined by the state of the system at the initial time and the present input to the system. In other words, the state of a dynamical system in general depends on both the present input to the system and the past history of the system. Even though it is often assumed that the state of a dynamical system is the *least* set of state variables needed to completely predict the effect of the past upon the future of the system, this is often a convenient simplifying assumption.

Ever since its inception, the basic questions concerning dynamical systems theory have involved qualitative solutions for the properties of a dynamical system; questions such as, For a particular initial system state, does the dynamical system have at least one solution? What are the asymptotic properties of the system solutions? How are the system solutions

[29] A Hausdorff space is a topological space in which there exists a pair of disjoint open neighborhoods for every pair of distinct points in the space.

dependent on the system initial conditions? How are the system solutions dependent on the form of the mathematical description of the dynamic of the system? How do system solutions depend on system parameters? And how do system solutions depend on the properties of the state space on which the system is defined?

Determining the mathematical rule or dynamic that defines the state of physical systems at a given future time from a given present state is one of the central problems of science. Once the flow or dynamic of a dynamical system describing the motion of the system starting from a given initial state is given, dynamical systems theory can be used to describe the behavior of the system states over time for different initial conditions. Throughout the centuries—from the great cosmic theorists of ancient Greece[30] to the present-day quest for a unified field theory—the most important dynamical system is our vicissitudinous universe. By using abstract mathematical models and attaching them to the physical world, astronomers, mathematicians, and physicists have used abstract thought to deduce something that is true about the natural system of the cosmos.

The quest by scientists, such as Brahe, Kepler, Galileo, Newton, Huygens, Euler, Lagrange, Laplace, and Maxwell, to understand the regularities inherent in the distances of the planets from the Sun and their periods and velocities of revolution around the Sun led to the science of dynamical systems as a branch of mathematical physics. Isaac Newton, however, was the first to model the motion of physical systems with differential equations. Newton's greatest achievement was the rediscovery that the motion of the planets and moons of the solar system resulted from a single fundamental source—the gravitational attraction of the heavenly

[30]The Hellenistic period (323–31 B.C.) spawned the scientific revolution leading to today's scientific method and scientific technology, including much of modern science and mathematics in its present formulation. Hellenistic scientists, which included Archimedes, Euclid, Eratosthenes, Eudoxus, Ktesibios, Philo, Apollonios, and many others, were the first to use abstract mathematical models and attach them to the physical world. More importantly, using abstract thought and rigorous mathematics (Euclidean geometry, real numbers, limits, definite integrals), these "modern minds in ancient bodies" were able to deduce complex solutions to practical problems and provide a deep understanding of nature. In his *Forgotten Revolution* [389] Russo convincingly argues that Hellenistic scientists were not just forerunners or anticipators of modern science and mathematics, but rather the true fathers of these disciplines. He goes on to show how science was born in the Hellenistic world and why it had to be reborn.

As in the case of the origins of much of modern science and mathematics, modern engineering can also be traced back to ancient Greece. Technological marvels included Ktesibios' pneumatics, Heron's automata, and arguably the greatest fundamental mechanical invention of all time—the Antikythera mechanism. The Antikythera mechanism, most likely inspired by Archimedes, was built around 76 B.C. and was a device for calculating the motions of the stars and planets, as well as for keeping time and calendar. This first analog computer involving a complex array of meshing gears was a quintessential hybrid dynamical system that unequivocally shows the singular sophistication, capabilities, and imagination of the ancient Greeks, and dispenses with the Western myth that the ancient Greeks developed mathematics but were incapable of creating scientific theories and scientific technology.

bodies. This discovery dates back to Aristarkhos' (310–230 B.C.) heliocentric theory of planetary motion and Hipparkhos' (190–120 B.C.) *dynamical* theory of planetary motion predicated on planetary attractions toward the Sun by a force that is inversely proportional to the square of the distance between the planets and the Sun [389, p. 304].

Many of the concepts of Newtonian mechanics, including relative motion, centrifugal and centripetal force, inertia, projectile motion, resistance, gravity, and the inverse square law, were known to the Hellenistic scientists [389]. For example, Hipparkhos' work *On bodies thrusting down because of gravity* (*Περὶ τῶν διὰ βαρύτητα κάτω φερομένων*) clearly and correctly describes the effects of gravity on projectile motion. And in Ploutarkhos' (46–120 A.D.) work *De facie quae in orbe lunae apparet* (*On the light glowing on the Moon*), he clearly describes the notion of gravitational interaction between heavenly bodies stating that "just as the sun attracts to itself the parts of which it consists, so does the earth ..."[31] [389, p. 304].

Newton himself wrote in his *Classical Scholia* [389, p. 376]: "Pythagoras ... applied to the heavens the proportions found through these experiments [on the pitch of sounds made by weighted strings], and learned from that the harmonies of the spheres. And so, by comparing those weights with the weights of the planets, and the intervals in sound with the intervals of the spheres, and the lengths of string with the distances of the planets [measured] from the center, he understood through the heavenly harmonies that the weights of the planets toward the sun ... are inversely proportional to the squares of their distances." And this admittance of the prior knowledge of the inverse square law predates Hooke's thoughts of explaining Kepler's laws out of the inverse square law communicated in a letter to Newton on January 6, 1680, by over two millennia.

It is important to stress here that what are erroneously called *Newton's laws of motion* in the literature were first discovered by Kepler, Galileo, and Descartes, with the latter first stating the law of inertia in its modern form. Namely, when viewed in an inertial reference frame, a body remains in the same state unless acted upon by a net force; and unconstrained motion follows a rectilinear path. Newton and Leibnitz independently advanced the basic dynamical tool invented two millennia earlier by Archimedes—the calculus;[32] with Euler being the first one to explicitly write down the second law of motion as an equation involving an applied force acting on

[31] ὣς γὰρ ὁ ἥλιος εἰς ἑαυτὸν ἐπιστρέφει τὰ μέρη ἐξ ὧν συνέστηκε, καὶ ἡ γῆ (in Ploutarkhos, *De facie quae in orbe lunae apparet*, 924E).

[32] In his treatise on *The Method of Mechanical Theorems* Archimedes (287–212 B.C.) established the foundations of integral calculus using infinitesimals, as well as the foundations of mathematical mechanics. In addition, in one of his problems he constructed the tangent at any given point for a spiral, establishing the origins of differential calculus [29, p. 32].

a body being equal to the time rate of change of its momentum. Newton, however, deduced a *physical* hypothesis—the law of universal gravitation involving an inverse-square law force—in precise mathematical form deriving (at the time) a cosmic dynamic using Euclidian geometry and *not* differential calculus (i.e., differential equations).

In his magnum opus, *Philosophiae Naturalis Principia Mathematica* [337], Newton investigated whether a small perturbation would make a particle moving in a plane around a center of attraction continue to move near the circle, or diverge from it. Newton used his analysis to analyze the motion of the moon orbiting the Earth. Numerous astronomers and mathematicians who followed made significant contributions to dynamical systems theory in an effort to show that the observed deviations of planets and satellites from fixed elliptical orbits were in agreement with Newton's principle of universal gravitation. Notable contributions include the work of Torricelli [443], Euler [137], Lagrange [256], Laplace [271], Dirichlet [116], Liouville [286], Maxwell [311], Routh [386], and Lyapunov [294–296].

Newtonian mechanics developed into the first field of modern science—dynamical systems as a branch of mathematical physics—wherein the circular, elliptical, and parabolic orbits of the heavenly bodies of our solar system were no longer fundamental determinants of motion, but rather approximations of the universal laws of the cosmos specified by governing differential equations of motion. And in the past century, dynamical systems theory has become one of the most fundamental fields of modern science as it provides the foundation for unlocking many of the mysteries in nature and the universe that involve the evolution of time. Dynamical systems theory is used to study ecological systems, geological systems, biological systems, economic systems, neural systems, and physical systems (e.g., mechanics, fluids, magnetic fields, galaxies), to cite but a few examples.

1.5 Dynamical Thermodynamics: A Postmodern Approach

In contrast to mechanics, which is based on a dynamical systems theory, classical thermodynamics (i.e., *thermostatics*) is a physical theory and does not possess equations of motion. Moreover, very little work has been done in obtaining extensions of thermodynamics for systems out of equilibrium. These extensions are commonly known as *thermodynamics of irreversible processes* or *modern irreversible thermodynamics* in the literature [113,367]. Such systems are driven by the continuous flow of matter and energy, are far from equilibrium, and often develop into a multitude of states. Connections between local thermodynamic subsystem interactions of these systems and the globally complex thermo*dynamical* system behavior are often elusive. This statement is true for nature in general and was most eloquently stated first by Herakleitos in his 123rd fragment—Φύσις κρύπτεσθαι φιλεί (Nature loves to hide).

These complex thermodynamic systems involve spatio-temporally evolving structures and can exhibit a hierarchy of emergent system properties. These systems are known as *dissipative systems* [195] and consume energy and matter while maintaining their stable structure by dissipating entropy to the environment. All living systems are dissipative systems; the converse, however, is not necessarily true. Dissipative living systems involve pattern interactions by which life emerges. This nonlinear interaction between the subsystems making up a living system is characterized by *autopoiesis* (self-creation). In the physical universe, billions of stars and galaxies interact to form self-organizing dissipative nonequilibrium structures [252, 369]. The fundamental common phenomenon among nonequilibrium (i.e., dynamical) systems is that they evolve in accordance with the laws of (nonequilibrium) thermodynamics.

Building on the work of nonequilibrium thermodynamic structures [166, 367], Sekimoto [400–404] introduced a stochastic thermodynamic framework predicated on Langevin dynamics in which fluctuation forces are described by Brownian motion. In this framework, the classical thermodynamic notions of heat, work, and entropy production are extended to the level of individual system trajectories of nonequilibrium ensembles. Specifically, system state trajectories are sample continuous and are characterized by a Langevin equation for each individual sample path and a Fokker-Planck equation for the entire ensemble of trajectories.

For such systems, energy conservation holds along fluctuating trajectories of the stochastic Markov process and the second law of thermodynamics is obtained as an ensemble property of the process. In particular, various fluctuation theorems [55, 56, 102, 103, 139, 153, 223, 229, 230, 255, 274, 401] are derived that constrain the probability distributions for the exchanged heat, mechanical work, and entropy production depending on the nature of the stochastic Langevin system dynamics.

Even though stochastic thermodynamics is applicable to a single realization of the Markov process under consideration with the first and second laws of thermodynamics holding for nonequilibrium systems, the framework only applies to multiple time-scale systems with a few observable slow degrees of freedom. The unobservable degrees of freedom are assumed to be fast, and hence, always constrained to the equilibrium manifold imposed by the instantaneous values of the observed slow degrees of freedom.

Furthermore, if some of the slow variables are not accessible, then the system dynamics are no longer Markovian. In this case, defining a system entropy is virtually impossible. In addition, it is unclear whether fluctuation theorems expressing symmetries of the probability distribution functions for thermodynamic quantities can be grouped into universal classes characterized by asymptotics of these distributions. Moreover, it is also unclear whether there exist system variables that satisfy the transitive equilibration property of the zeroth law of thermodynamics for nonequilibrium stochastic thermodynamic systems.

In an attempt to create a generalized theory of evolution mechanics by unifying classical mechanics with thermodynamics, the authors in [25, 26, 423, 424] developed a framework of system thermodynamics based on the concept of *tribo-fatigue entropy*. This framework, known as *damage mechanics* [25, 26] or *mechanothermodynamics* [423, 424], involves an irreversible entropy function along with its generation rate that captures and quantifies system aging. Specifically, the second law is formulated analytically for organic and inorganic bodies, and the system entropy is determined by a damageability process predicated on mechanical and thermodynamic effects resulting in system state changes.

In [195], the authors develop a postmodern framework for thermodynamics that involves open interconnected dynamical systems that exchange matter and energy with their environment in accordance with the first law (conservation of energy) and the second law (nonconservation of entropy) of thermodynamics. Symmetry can spontaneously occur in such systems by invoking the two fundamental axioms of the science of heat.

Namely, *i*) if the energies in the connected subsystems of an interconnected system are equal, then energy exchange between these subsystems is not possible, and *ii*) energy flows from more energetic subsystems to less energetic subsystems. These axioms establish the existence of a *global* system entropy function as well as *equipartition of energy* [195] in system thermodynamics; an *emergent* behavior in thermodynamic systems. Hence, in complex interconnected thermodynamic systems, higher symmetry (i.e., system decomplexification) is not a property of the system's parts but rather emerges as a result of the nonlinear subsystem interactions.

The goal of the present monograph is directed toward building on the results of [195] to place thermodynamics on a system-theoretic foundation by combining the two universalisms of thermodynamics and dynamical systems theory under a single umbrella so as to harmonize it with classical mechanics. In particular, we develop a novel formulation of thermodynamics that can be viewed as a moderate-sized dynamical systems theory as compared to statistical thermodynamics. This middleground theory involves large-scale dynamical system models characterized by ordinary deterministic and stochastic differential equations, as well as infinite-dimensional models characterized by partial differential equations and functional delay differential equations that bridge the gap between classical and statistical thermodynamics.

Specifically, since thermodynamic models are concerned with energy flow among subsystems, we use a state space formulation to develop a nonlinear compartmental dynamical system model that is characterized by energy conservation laws capturing the exchange of energy and matter between coupled macroscopic subsystems. Furthermore, using graph-theoretic notions, we state two thermodynamic axioms consistent with the zeroth and second laws of thermodynamics, which ensure that our large-scale dynamical system model gives rise to a thermodynamically consistent energy flow model. Specifically, using a large-scale dynamical systems theory perspective for thermodynamics, we show that our compartmental dynamical system model leads to a precise formulation of the equivalence between work energy and heat in a large-scale dynamical system.

Since our dynamical thermodynamic formulation is based on a large-scale dynamical systems theory involving the exchange of energy with conservation laws describing transfer, accumulation, and dissipation between subsystems and the environment, our framework goes beyond classical thermodynamics characterized by a purely empirical theory, wherein a physical system is viewed as an input-output *black box* system. Furthermore, unlike classical thermodynamics, which is limited to the description of systems in equilibrium states, our approach addresses nonequilibrium thermodynamic systems. This allows us to connect and unify the behavior of heat as described by the equations of thermal transfer and as described by classical thermodynamics. This exposition further demonstrates that these disciplines of classical physics are derivable from the same principles and are part of the same scientific and mathematical framework.

Our nonequilibrium thermodynamic framework goes beyond classical irreversible thermodynamics developed by Onsager [347, 348] and further extended by Casimir [82] and Prigogine [166, 367, 368], which, as discussed in Section 1.3, fall short of a complete dynamical theory. Specifically, their theories postulate that the local instantaneous thermodynamic variables of the system are the same as that of the system in equilibrium. This implies that the system entropy in a neighborhood of an equilibrium is dependent on the same variables as those at equilibrium, violating Gibbs' maximum entropy principle. In contrast, the proposed system thermodynamic formalism brings classical thermodynamics within the framework of modern nonlinear dynamical systems theory, thus providing information about the dynamical behavior of the thermodynamic state variables between the initial and final equilibrium system states.

Next, we give a deterministic definition of entropy for a large-scale dynamical system that is consistent with the classical thermodynamic definition of entropy, and we show that it satisfies a Clausius-type inequality leading to the law of entropy nonconservation. However, unlike classical thermodynamics, wherein entropy is not defined for arbitrary states out of equilibrium, our definition of entropy holds for nonequilibrium dynamical systems.

Furthermore, we introduce a *new* and dual notion to entropy—namely, *ectropy*[33]—as a measure of the tendency of a large-scale dynamical system to do useful work and grow more organized, and we show that conservation of energy in an adiabatically isolated thermodynamically consistent system necessarily leads to nonconservation of ectropy and entropy. Hence, for every dynamical transformation in an adiabatically isolated thermodynamically consistent system, the entropy of the final system state is greater than or equal to the entropy of the initial system state.

Then, using the system ectropy as a Lyapunov function candidate, we show that in the absence of energy exchange with the environment our thermodynamically consistent large-scale nonlinear dynamical system model possesses a continuum of equilibria and is *semistable*, that is, it has convergent subsystem energies to Lyapunov stable energy equilibria determined by the large-scale system initial subsystem energies. In addition, we show that the steady-state distribution of the large-scale system energies is uniform, leading to system energy equipartitioning corresponding to a minimum ectropy and a maximum entropy equilibrium state.

For our thermodynamically consistent dynamical system model, we further establish the existence of a *unique* continuously differentiable *global* entropy and ectropy function for all equilibrium and nonequilibrium states. Using these global entropy and ectropy functions, we go on to establish a clear connection between thermodynamics and the arrow of time. Specifically, we rigorously show a *state irrecoverability* and hence a *state irreversibility*[34] nature of thermodynamics. In particular, we show that for

[33]Ectropy comes from the Greek word $\varepsilon\kappa\tau\rho o\pi\eta$ ($\varepsilon\kappa$ and $\tau\rho o\pi\eta$) for outward transformation connoting evolution or complexification and is the literal antonym of entropy ($\varepsilon\nu\tau\rho o\pi\eta$—$\varepsilon\nu$ and $\tau\rho o\pi\eta$), signifying an inward transformation connoting devolution or decomplexification. The word *entropy* was proposed by Clausius for its phonetic similarity to energy with the additional connotation reflecting change ($\tau\rho o\pi\eta$).

[34]In the terminology of [448], state irreversibility is referred to as *time-reversal non-invariance*. However, since the term *time reversal* is not meant literally (that is, we consider dynamical systems whose trajectory reversal is or is not allowed and *not* a reversal of time itself), state reversibility is a more appropriate expression. And in that regard, a more appropriate expression for the arrow

every nonequilibrium system state and corresponding system trajectory of our thermodynamically consistent large-scale nonlinear dynamical system, there does not exist a state such that the corresponding system trajectory completely recovers the initial system state of the dynamical system and at the same time restores the energy supplied by the environment back to its original condition.

This, along with the existence of a global strictly increasing entropy function on every nontrivial system trajectory, gives a clear *time-reversal asymmetry* characterization of thermodynamics, establishing an emergence of the direction of time flow. In the case where the subsystem energies are proportional to subsystem temperatures, we show that our dynamical system model leads to temperature equipartition, wherein all the system energy is transferred into heat at a uniform temperature. Furthermore, we show that our system-theoretic definition of entropy and the newly proposed notion of ectropy are consistent with Boltzmann's kinetic theory of gases involving an n-body theory of ideal gases divided by diathermal walls. Finally, these results are generalized to continuum thermodynamics, stochastic thermodynamics, and relativistic thermodynamics involving infinite-dimensional, Markovian, and functional energy flow conservation models.

1.6 A Brief Outline of the Monograph

The objective of this monograph is to develop a system-theoretic foundation for thermodynamics using dynamical systems and control notions. The main contents of the monograph are as follows. In Chapter 2, we establish notation and definitions, and we develop several key results on nonnegative and compartmental dynamical systems needed to establish thermodynamically consistent energy flow models. Furthermore, we introduce the notions of (ir)reversible and (ir)recoverable dynamical systems, volume-preserving flows and recurrent dynamical systems, as well as output reversibility in dynamical systems.

In Chapter 3, we use a large-scale dynamical systems perspective to provide a system-theoretic foundation for thermodynamics. Specifically, using a system state space formulation, we develop a nonlinear compartmental dynamical system model characterized by energy conservation laws that is consistent with basic thermodynamic principles. In particular, using the total subsystem energies as a candidate system energy storage function, we show that our thermodynamic system is *lossless*, and hence, can deliver to its surroundings all of its stored subsystem energies and can store all of the work done to all of its subsystems. This leads to the first law of

of time is *system degeneration over time* signifying irrecoverable system changes.

thermodynamics involving conservation of energy and places no limitation on the possibility of transforming heat into work or work into heat.

Next, we show that the classical Clausius equality and inequality for reversible and irreversible thermodynamics are satisfied over cyclic motions for our thermodynamically consistent energy flow model and guarantee the existence of a continuous system entropy function. In addition, we establish the existence of a *unique*, continuously differentiable *global* entropy function for our large-scale dynamical system, which is used to define inverse subsystem temperatures as the derivative of the subsystem entropies with respect to the subsystem energies.

Then we turn our attention to stability and convergence. Specifically, using the system ectropy as a Lyapunov function candidate, we show that in the absence of energy exchange with the environment, the proposed thermodynamic model is semistable with a uniform energy distribution corresponding to a state of minimum ectropy and a state of maximum entropy. Furthermore, using the system entropy and ectropy functions, we develop a clear connection between irreversibility, the second law of thermodynamics, and the entropic arrow of time.

In Chapter 4, we generalize the results of Chapter 3 to the case where the subsystem energies in the large-scale dynamical system model are proportional to subsystem temperatures, and we arrive at temperature equipartition for the proposed thermodynamic model. Furthermore, we provide a kinetic theory interpretation of the steady-state expressions for entropy and ectropy. Moreover, we establish connections between dynamical thermodynamics and classical thermodynamics.

In Chapter 5, we augment our nonlinear compartmental dynamical system model with an additional (deformation) state representing compartmental volumes to arrive at a general statement of the first law of thermodynamics, giving a precise formulation of the equivalence between heat and mechanical work. Furthermore, we define the Gibbs free energy, Helmholtz free energy, and enthalpy functions for our large-scale system thermodynamic model. In addition, we use the proposed augmented nonlinear compartmental dynamical system model in conjunction with a Carnot-like cycle analysis to show the equivalence between the classical Kelvin and Clausius postulates of the second law of thermodynamics.

In Chapter 6, we address the problems of nonnegativity, realizability, reducibility, and semistability of chemical reaction networks. Specifically, we show that mass-action kinetics have nonnegative solutions for initially nonnegative concentrations, we provide a general procedure for reducing the dimensionality of the kinetic equations, and we present stability results based upon Lyapunov methods. Furthermore, we present a state space dynamical system model for chemical thermodynamics. In particular, we use the law of mass action to obtain the dynamics of chemical reaction networks.

In addition, using the notion of the chemical potential, we unify our state space mass-action kinetics model with our dynamical thermodynamic system model involving system energy exchange. Moreover, we show that entropy production during chemical reactions is nonnegative and the dynamical system states of our chemical thermodynamic state space model converge to a state of temperature equipartition and zero affinity (i.e., the difference between the chemical potential of the reactants and the chemical potential of the products in a chemical reaction).

In Chapter 7, we merge the theories of semistability and finite-time stability to develop a rigorous framework for finite-time thermodynamics. Specifically, using a geometric description of homogeneity theory, we develop intercompartmental energy flow laws that guarantee finite-time semistability and energy equipartition for the thermodynamically consistent model developed in Chapter 3.

Next, in Chapter 8, we address the problem of thermodynamic critical phenomena and continuous phase transitions. In particular, to address discontinuities in the derivatives of the thermodynamic state quantities, we consider dynamical systems with Lebesgue measurable and locally essentially bounded vector fields characterized by differential inclusions involving Filippov set-valued maps specifying a set of directions for the system generalized velocities and admitting Filippov solutions with absolutely continuous curves. Moreover, we present Lyapunov-based tests for semistability, finite-time semistability, and energy equipartition for a discontinuous power balance thermodynamic model characterized by differential inclusions.

In Chapter 9, we develop thermodynamic models for discrete-time, large-scale dynamical systems. Specifically, using a framework analogous to Chapter 3, we develop energy flow models possessing discrete energy conservation, energy equipartition, temperature equipartition, and entropy nonconservation principles for discrete-time, large-scale dynamical systems.

To address thermodynamic critical phenomena and discontinuous phase transitions, in Chapter 10 we combine the frameworks of Chapters 3 and 9 to develop hybrid thermodynamic models. Specifically, to capture jump discontinuities in the fundamental thermodynamic state quantities, we develop a hybrid large-scale dynamical system using impulsive compartmental and thermodynamic dynamical system models involving an interacting mixture of continuous and discrete dynamics exhibiting discontinuous flows on appropriate manifolds.

In Chapter 11, we extend the results of Chapter 3 to continuum thermodynamic systems, wherein the subsystems are uniformly distributed over an n-dimensional (not necessarily Euclidean) space. Specifically, we develop a nonlinear distributed-parameter model wherein the system energy is modeled by a conservation equation in the form of a nonlinear partial differential equation. Energy equipartition and semistability are shown using Sobolev embedding theorems and the notion of generalized (or weak) solutions. This exposition shows that the behavior of heat, as described by the equations of thermal transport and as described by classical thermodynamics, is derivable from the same principles and is part of the same scientific discipline, and thus provides a unification between Fourier's theory of heat conduction and classical thermodynamics.

In Chapter 12, we extend the results of Chapter 3 to large-scale dynamical systems driven by Markov diffusion processes to present a unified framework for statistical thermodynamics predicated on a stochastic dynamical systems formalism. Specifically, using a stochastic state space formulation, we develop a nonlinear stochastic compartmental dynamical system model characterized by energy conservation laws that is consistent with statistical thermodynamic principles. In particular, we show that the average stored system energy for our stochastic thermodynamic model is a martingale with respect to the system filtration and is equal to the mean energy that can be extracted from the system and the mean energy that can be delivered to the system in order to transfer it from a zero energy level to an arbitrary nonempty subset in the state space over a finite stopping time.

Next, to effectively address the universality of thermodynamics and the arrow of time to cosmology, we extend our dynamical systems framework of thermodynamics to include relativistic effects. To this end, in Chapter 13 we give a brief exposition of the special and general theories of relativity, and review some basic concepts on relativistic kinematics and relativistic dynamics.

Then, in Chapter 14, we extend our results to thermodynamic systems that are moving relative to a local observer moving with the system and a fixed observer with respect to which the system is in motion. Furthermore, thermodynamic effects in the presence of a strong gravitational field are also discussed. In addition, using the topological isomorphism between entropy and time established in Chapter 3 and Einstein's time dilation assertion that increasing an object's speed through space results in decreasing the object's speed through time, we present an entropy dilation principle, which shows that the change in entropy of a thermodynamic system decreases as the system's speed increases through space.

To account for finite subluminal speed of heat propagation, in Chapter 15 we generalize the results of Chapter 3 to general thermodynamic compartmental systems that account for energy and matter in transit between compartments. Specifically, we develop thermodynamic models that guarantee conservation of energy, semistability, and state equipartitioning with directed and undirected thermal flow as well as flow delays between compartments.

Finally, we draw conclusions in Chapter 16, and in Chapter 17, we present a high-level scientific discussion of several peripheral, albeit key areas of how our dynamical systems framework of thermodynamics can be used to foster the development of new frameworks in explaining the fundamental thermodynamic processes occurring in nature, explore new hypotheses that challenge the use of classical thermodynamics, and develop new assertions that can provide deeper insights into the constitutive mechanisms that describe the acute microcosms and macrocosms of science.

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