# Chapter One

# Introduction

## 1.1 An Overview of 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 and work 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. Hence, 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 refers to changes in the status quo of the system and is a measure of molecular 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 [70, 89, 105], flows on 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 as well as nuclear explosions, 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 flexuous history; see [19, 23, 32, 41, 45, 77, 94, 96, 99].

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. 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 (conservation) equation in the form of a *parabolic* partial differential equation. Such systems are infinite-dimensional, and hence, finite-dimensional approximations are of very high order, giving rise to large-scale dynamical systems. Since energy is a fundamental concept in the analysis of large-scale dynamical systems, and heat (energy) 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.

High-dimensional dynamical systems can arise from both macroscopic and *microscopic* points of view. Microscopic thermodynamic

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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 derivation 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 (∼ 535–∼ 475 B.C.). Herakleitos' profound statements (quoted in ancient Greek on page vi), *Everything is in a state of flux* 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 physics and metaphysics. The idea that the universe is in constant change and that there is an underlying order to this change—the *Logos*, dare we say—postulates the very existence of entropy as a physical property of matter permeating the whole of nature and the universe.

models can have the form of a distributed-parameter model or a large-scale system model comprised of a large number of interconnected subsystems. In contrast to macroscopic models involving the evolution of global quantities (e.g., energy, temperature, entropy, etc.), 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 microscopic 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, 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.

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] and its laws have become one of the most firmly established scientific achievements ever accomplished. The pioneering work of Carnot [24] was the first to establish the impossibility of a *perpetuum mobile* of the second kind[4] by constructing a cyclical process

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[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 Rankine, Reech, Clapeyron, 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.

(now known as the Carnot cycle) involving two competing cycles, 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—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 only a function of the temperatures of the boiler and the cooler. 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 was remarkably arrived at using the erroneous concept that heat is an indestructible substance, that is, the *caloric theory of heat*.[5]

Using a macroscopic approach and building on the work of Carnot, Clausius [26–29] was the first to introduce the notion of entropy as a physical property of matter and to establish the two main laws of thermodynamics involving conservation of energy[6] and nonconservation of entropy. Specifically, using conservation of energy principles, Clausius showed that Carnot's principle is valid. Furthermore, Clausius postulated that it is impossible to 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 ap-

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[5] 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 1870's, 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.

[6] Even though many scientists are credited with the law of conservation of energy, it was first discovered independently by Mayer and Joule, with Joule providing a series of decisive, quantitative studies in the 1840's showing the equivalence between heat and mechanical work.

proach a limiting state. 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.[7] In his later work [29], Clausius remitted his famous claim that the entropy of the universe is tending to a maximum.

In parallel research Kelvin [55, 93] 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.[8] Without any supporting mathematical arguments, Kelvin goes on to state that the universe is heading towards a state of eternal rest wherein all life on Earth in the distant future shall perish. This claim by Kelvin involving a universal tendency towards dissipation has come to be known as the *heat death of the universe*.

Building on the work of Clausius and Kelvin, Planck [82,83] refined the formulation of classical thermodynamics. From 1897 to 1964, Planck's treatise [82] underwent eleven editions. Nevertheless, these editions have several inconsistencies regarding key notions and definitions of reversible and irreversible processes. 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

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[7] 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. 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 space-time need to be accounted for. In this case, the energy density tensor in Einstein's equations is only covariantly conserved since it does not account for gravitational energy—an unsolved problem in the general theory of relativity. Nevertheless, the law of conservation of energy is as close to an absolute truth as our incomprehensible universe will allow us to deduce.

[8] 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 with negative absolute temperatures are discussed in [71, 86].

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.

Unlike the work of Clausius, Kelvin, and Planck involving cyclical system transformations, the work of Gibbs [39] 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*[9] (i.e., a system with no energy exchange with the environment) is in equilibrium if and only if all possible variations of the state of the system that do not alter its energy, the variation of the system entropy is negative semidefinite. Hence, Gibbs' principle gives necessary and sufficient conditions for a thermodynamically stable equilibrium and should be viewed as a variational principle defining admissible (i.e., stable) equilibrium states. Thus, it does not provide any information about the dynamical state of the system as a function of time nor any conclusion regarding entropy increase in a dynamical system transformation.

Carathéodory [20, 21] 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[10] is used such that an empirical statement of the second law characterizes a mathematical structure for an abstract state space. Carathéodory's postulate for the second law states that in every open neighborhood of any state of a system, there exist states such that for some second open neighborhood contained in the first neighborhood, all the states in the second neighborhood cannot be reached by adiabatic processes from states in the first neighborhood. From this postulate Carathéodory goes on to show

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[9] 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.

[10] Carathéodory's definition of an adiabatic process is nonstandard and involves transformations that take place while the system remains in an *adiabatic container*. For details see [20, 21].

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. One of the key weaknesses 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 [15] 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 individual atoms are assumed to obey the laws of Newtonian mechanics, by suitably averaging over the velocity distribution of these atoms Boltzmann showed how 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).

In the first half of the twentieth century, the macroscopic and microscopic 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 [5,19,96]. 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 towards equilibrium states as a consequence of the law of entropy increase! Furthermore, classical thermodynamics is mainly 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 external disturbance 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 [96, p. 6], wherein Truesdell describes the present state of the theory of thermodynamics as a "dismal swamp of obscurity." More recently, Arnold [5, 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, 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 Clausius, Kelvin, Planck, and Carathéodory have very different meanings. In particular, Clausius defines a reversible (*umkehrbar*) process as a slowly varying process wherein successive states of this process differ by infinitesimals from the equilibrium system states. Such system transformations are commonly referred to as *quasistatic* transformations in the thermodynamic literature. Alternatively, Kelvin's notions of reversibility involve the ability of a system to completely recover its initial state from the final system state. 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 [16, 97], with [97] providing an excellent exposition of the relation between irreversibility, the second law of thermodynamics, and the arrow of time.

The arrow of time[11] remains one of physics' most perplexing enigmas [36,43,53,60,69,83,87,102]. Even though time is one of the most familiar concepts humankind has ever encountered, it is the least understood. Puzzling questions of time's mysteries have remained unanswered throughout the centuries. 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 is forever flowing towards 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.[12] In this regard, thermodynamics is disjoint from Newtonian and Hamiltonian mechanics (including Einstein's 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 [61]. For example, 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. The idea that the second law of thermodynamics provides a physical foundation for the arrow

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[11] 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.

[12] 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.

of time has been postulated by many authors [37, 85, 87]. However, a convincing argument of this claim has never been given [43, 60, 97].

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 [31, 75, 95]. 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 [30, 34, 35, 44]. 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.

More recently, a major contribution to equilibrium thermodynamics is given in [65]. This work builds on the work of Carathéodory [20, 21] and Giles [40] 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 [65] 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 [65] is not equivalent to that of Carathéodory's notion of a simple system. Connections between thermodynamics and system theory as well as information theory have also been explored in the literature [9, 10, 17, 18, 48, 80, 100, 102, 104, 106]. For an excellent exposition of these different facets of thermodynamics see [42].

Thermodynamic principles have also been repeatedly used in coupled mechanical systems to arrive at energy flow models with modal energy playing the role of temperature. Specifically, in an attempt to approximate high-dimensional dynamics of large-scale structural (oscillatory) systems with a low-dimensional diffusive (non-oscillatory) 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 [22, 54, 62, 69, 91, 103]. 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.

Alternatively, a deterministic thermodynamically motivated energy flow modeling for structural systems is addressed in [57–59]. 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 [10]. 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 [10]. With the notable exception of [22], none of the aforementioned SEA-related works addresses the second law of thermodynamics involving entropy notions in the energy flow between subsystems.

## 1.2 System Thermodynamics

In contrast to mechanics, which is based on a dynamical system theory, classical thermodynamics is a physical theory and does not possess equations of motion. The goal of the present monograph is directed towards placing thermodynamics on a system-theoretic foundation 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 system theory as compared to statistical thermodynamics. This middle-ground theory involves deterministic large-scale dynamical system models 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 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 thermodynamic formulation is based on a large-scale dynamical system 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 often 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 demonstrates that these disciplines of classical physics are derivable from the same principles and are part of the same mathematical framework.

Our nonequilibrium thermodynamic framework goes beyond the reciprocal relations for irreversible processes developed by Onsager[13] [78, 79] and further extended by Casimir [25], which fall short of a complete dynamical theory. 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 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 between the initial and final equilibrium system states.

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[13] 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.

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*[14]—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*[15] nature of thermodynamics.

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[14] Ectropy comes from the Greek word $\varepsilon\kappa\tau\rho o\pi\eta$ ($\varepsilon\kappa$ and $\tau\rho o\pi\eta$) for outward transformation 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. The word *entropy* was proposed by Clausius for its phonetic similarity to energy with the additional connotation reflecting change ($\tau\rho o\pi\eta$) and does not necessarily correspond to an inward or outward change.

[15] In the terminology of [97], 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.

In particular, we show that for 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 involving infinite-dimensional energy flow conservation models.

## 1.3 A Brief Outline of the Monograph

The objective of this monograph is to develop a system-theoretic foundation for classical 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 review some basic 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, as well as volume-preserving flows and recurrent dynamical systems. In Chapter 3, we use a large-scale dynamical systems perspective to provide a system-theoretic foundation for thermodynamics. Specifically, using a 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 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. 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 work. 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-Planck and Clausius postulates of the second law of thermodynamics. In Chapter 6, we specialize the results of Chapter 3 to thermodynamic systems with linear energy exchange.

In Chapter 7, 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 diffusion (conservation) equation in the form of a parabolic partial differential equation. Energy equipartition and semistability are shown using the well-known 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. Finally, we draw conclusions in Chapter 8.