We dedicate this book
to our teacher of thermodynamics,
George N. Hatsopoulos

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$$s(T,p) = a\ln T + bT + \tfrac{1}{2}cT^2 + \tfrac{1}{3}dT^3 - R\ln p$$

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Preface

"In view of the large number of books on thermodynamics it may seem surprising that there should be any need for yet another," wrote Guggenheim in the preface of his book "Thermodynamics" in 1949. Many more books on thermodynamics have been published since then. So, why are we adding ours to the long list of entries on the subject?

During the past two decades of teaching thermodynamics to students from all over the globe, we have sensed a widespread quest for more clarity, unambiguity, and logical consistency in the exposition of the foundations than are available in traditional presentations. In response to our students' demand, we have gradually developed a set of arguments, observations, definitions, statements, and derivations that cannot be found in any of the books currently available. Continuing the effort pioneered by Keenan and Hatsopoulos, we have composed an exposition of the foundations and the applications of thermodynamics that many enthusiastic M.I.T. students have found clarifying, rewarding, and inspiring. Our class notes have grown into a coherent collection thoroughly tested in the classroom, equipped with a large number of homework problems, and mature enough for wider dissemination.

In the preface of his book "Concepts of Thermodynamics" in 1960, Obert wrote: "Most teachers will agree that the subject of engineering thermodynamics is confusing to the student, despite the simplicity of the usual undergraduate presentation." In our experience, the major source of confusion is the lack of logical consistency and completeness in the many presentations of the foundations of thermodynamics. The definition of a system as just "the subject of analysis" or "anything that is enclosed by a surface in space" is incomplete. The definition of properties in terms of the state is circular if the definition of state is in terms of the properties. The definition of heat as anything that is not work is incomplete and ambiguous. The definition of thermal equilibrium in terms of temperature is circular if the definition of temperature is in terms of thermal equilibrium. The restriction to equilibrium states is artificial if the purpose is the use of heat and cycles to define entropy. Even if entirely uninterested in the foundations, the student cannot avoid but sense this ambiguity and lack of logical consistency and develop the incorrect conviction that thermodynamics is a confusing, ambiguous, handwaving subject. Unfortunately, such a conviction is quite widespread and very difficult to dismantle.

The problem is not resolved even by recent books for engineering students such as the excellent textbooks on thermodynamics by F. F. Huang (1988 edition), K. Wark, Jr. (1988 edition), and M. J. Moran and H. N. Shapiro (1988), which tend to deemphasize the subtleties of the foundations by placing the emphasis on the applications of energy and entropy balances. The student encounters no difficulty in mastering the mechanics of energy and entropy balances. But the conviction that thermodynamics is based on ambiguous grounds remains. In our view, this hinders comprehension and discourages any desire to further explore and exploit the wide range of implications and applications of the subject.

In the novel exposition of the foundations that we present, we strive to develop each of the basic concepts in full detail and without ambiguities, at a level that assumes a sophomore background in calculus and elementary physics. Some characteristic features are as follows.

- The basic concepts and principles are introduced in a novel logical sequence that eliminates the traditional problem of incomplete definitions and vicious circles.
- The carefully worded statements of the laws of thermodynamics are presented as fundamental laws of physics that complement the laws of dynamics.
- The principles and results are developed for both macroscopic and microscopic systems, and for both equilibrium and nonequilibrium states.
- The concept of entropy is defined for any system, including a system with a single degree of freedom, and for any state, including a nonequilibrium state.
- The state principle is derived as an exact and rigorous result valid for any stable equilibrium state of any system.
- The concept of temperature is defined for the stable equilibrium states of any system, including a system consisting of one particle with a single degree of freedom.
- The concepts of work and heat are defined in terms of the concepts of energy and entropy exchanges and not vice versa.
- The third law is introduced in a novel discussion of the lowest-temperature stable equilibrium states.
- The principles and results are illustrated pictorially on a novel graph of energy versus entropy.
- A concise but precise summary of the foundations (Chapter 14) provides a suitable starting point for a first introductory undergraduate course.
- The validity of the Euler relation for relatively large values of the amounts of constituents is derived from a rigorous and novel definition of a simple system.
- The derivations of relations among properties of simple systems are made easy to follow by showing explicitly all the functional dependences.
- The chemical equilibrium equation is derived from a rigorous and novel discussion based on the definition of a simple system.
- The typical end-of-chapter problems that test each new concept are complemented by a large number of more structured problems designed to test the connections between new concepts and concepts introduced in earlier chapters.

A part of the book is intended for use as a text for an introductory undergraduate course in thermodynamics. Other parts provide material for more advanced courses, including a graduate course with emphasis on the foundations. We discuss suggestions for this partitioning at the end of Chapter 1.

In Chapter 1 we describe some salient features of the models of physical phenomena without concern as to the precise meanings of the terms we use. Our aim is to motivate the reader to pursue a systematic study of the applications and a deeper scrutiny of the foundations of thermodynamics. For this pursuit, at the end of the chapter we outline four different alternative paths to a study of thermodynamics using this book: an introductory undergraduate path, an advanced undergraduate path with emphasis on applications, a graduate path with emphasis on advanced topics, and a graduate path with emphasis on the general foundations. For each path we suggest the study of different chapters.

In Chapters 2 to 13 we discuss the key concepts and fundamental principles of thermodynamics. In doing so, we assume that concepts and principles such as space, time, reference frame, velocity, acceleration, force, mass, force field, gravitational acceleration, electrostatic field, magnetic field, momentum, kinetic energy, potential energy, Newton's laws, and Maxwell's equations are all part of the educational background of our reader in mechanics and electromagnetism at an advanced high school or introductory college level. We require this background not because we discuss any complicated issues of these facets of natural science but because it is part of the conceptual underpinning of thermodynamics.

In Chapter 2 we begin our detailed exposition of the foundations with kinematics and dynamics. In kinematics we discuss the definitions of system, property, and state. Our definitions eliminate the consideration of all the statistical arguments that lurk under all traditional expositions of thermodynamics. The concept of state that we define provides a common thread for the unification of the various branches of physics without need to modify its meaning from branch to branch. The state is the set of instantaneous values of all the amounts of constituents, all the parameters that characterize the external forces, and all the properties. Without alteration, this definition is valid for any system, macroscopic or microscopic, and any condition, changing or not changing with time.

In dynamics we discuss spontaneous and induced changes of state as functions of time, that is, we introduce the idea of the equation of motion of a system. Certain time evolutions obey Newton's equation of motion or its quantum-mechanical equivalent, the Schrödinger equation of motion. Other experimentally observed time evolutions, however, do not obey either of these equations. So the equations of motion that we have are incomplete. The discovery of the complete equation of motion that describes all physical phenomena remains a subject of research at the frontier of science—one of the most intriguing and challenging problems in physics. Among the many features of the equation of motion that have already been discovered, the most general and well established are captured by the statements of the first and the second laws of thermodynamics. From these laws we derive powerful tools for analyses of time-dependent phenomena. We discuss the two laws in Chapters 3 and 4. We conclude Chapter 2 with definitions of isolation, mode of interaction, and process.

In Chapter 3 we introduce a carefully worded and unambiguous statement of the first law in terms of the concept of state and the definition of a weight process. One of the principal implications of this statement is the existence of the property that we call energy and denote by E. Energy is defined for all systems and all states, and is an additive property. It obeys a conservation principle, that is, it remains invariant in the course of spontaneous changes of state of an isolated system. Because changes of state require a finite time to occur, the principle of energy conservation implied by the first law is an aspect of time evolution. As such, it reflects a special feature of the general equation of motion, even though the equation itself remains to be discovered.

We conclude Chapter 3 with a discussion of other implications of the first law: the impossibility of a perpetual-motion machine of the first kind, the relation of the law to special relativity and mass, and the energy balance. The energy balance is the most universal and powerful tool used in the analysis of practically every physical phenomenon.

In Chapter 4 we recognize that at each instant of time a system can be found in one of many different states. We classify each state according to its time evolution and define unsteady, steady, nonequilibrium, unstable equilibrium, metastable equilibrium, and stable equilibrium states.

We recall that equilibrium is not always stable and raise the question: Among all the states of a system that correspond to a given value of energy, are there any that are stable equilibrium? Close scrutiny of this question reveals that the answer cannot be found by means of the theory of mechanics. Yet experience shows that such stable equilibrium states exist. The answer is provided by the second law of thermodynamics. We introduce a carefully worded and unambiguous statement of the second law in terms of the concepts of energy, stable equilibrium state, and reversible process. This statement is an outgrowth of the pioneering work by Hatsopoulos and Keenan. In due course, we show that it entails all correct statements of the second law that have appeared in the literature. We emphasize that the second law implies the existence of stable equilibrium states but does not require that all states be stable equilibrium. Indeed, the vast majority of states are not stable equilibrium. The requirement that some equilibrium states must be stable reflects a most important feature of the general equation of motion, even though this equation remains to be discovered.

The two laws of thermodynamics have many important and practical implications. One of these implications, deduced in Chapter 4, is the impossibility of a perpetual-motion machine of the second kind. Other implications are explored in Chapters 5 to 12.

In Chapter 5 we show that, in general, not all the energy of a system can be transferred to a weight in a gravity field. Under the broad restrictions that define a weight process, the amount of energy that can be transferred from a system to a weight depends on the state of the system. If it is not a stable equilibrium state, at least a fraction of the energy can be transferred to the weight. But if it is a stable equilibrium state, no energy can be transferred to the weight. This limitation reflects innumerable experimental observations, but cannot be accounted for by the principles of mechanics alone. It is one of the important implications of the two laws of thermodynamics.

We conclude Chapter 5 with a proof of the existence of a novel important property that we call generalized adiabatic availability and denote by Ψ. The generalized adiabatic availability of a system in a given state is related to the optimum amount of energy that can be exchanged between the system and a weight in a weight process. Like energy, this property is well defined for all systems and all states.

In Chapter 6 we introduce a special reference system, called a reservoir, and discuss the possible weight processes that the composite of a system and a reservoir may experience. We prove the existence of another important property that we call generalized available energy with respect to a given reservoir and denote by Ω^R. The generalized available energy of a system in a given state is related to the generalized adiabatic availability of the composite of the system and the reservoir. Like energy and generalized adiabatic availability, Ω^R is a property that is well defined for all systems and all states. It is a generalization of the concept of motive power of fire first introduced by Carnot.

In Chapter 7 we disclose the existence of the property that we call entropy and denote by S. Entropy is defined in terms of energy, generalized available energy with respect to an arbitrarily selected reservoir, and a constant that depends on the reservoir. In terms of symbols the definition is

$$S = S_0 + \frac{1}{c_R}\left[(E - E_0) - (\Omega^R - \Omega_0^R)\right]$$

where E_0 and Ω_0^R refer to an arbitrary reference state, S_0 is a constant fixed once and for all for the system, and the constant c_R is a carefully defined property of the reservoir. The definition appears to depend on the selection of the reservoir. However, we prove that the role of the reservoir is only auxiliary, that is, that the value of S is independent of any characteristics of the arbitrarily selected reservoir. Because both E and Ω^R are defined for all systems (macroscopic as well as microscopic) and all states (equilibrium as well as not equilibrium), S is also defined for all systems and all states, including a system with one degree of freedom in any of its states. The concept of entropy introduced here differs from and is more general than that of most textbooks, where, as Herbert B. Callen stresses in his "Thermodynamics," "the existence of the entropy" is postulated "only for equilibrium states" and the "postulate makes no reference whatsoever to nonequilibrium states."

A discussion of the main features of entropy completes Chapter 7. We show that entropy obeys a principle of nondecrease, that is, it either remains invariant or increases in the course of spontaneous changes of state of an isolated system. We show that the entropy increases if a spontaneous process is irreversible, and we call such increase a creation or generation of entropy within the system. Like the principle of energy conservation, the principle of nondecrease of entropy is an aspect of the time evolution and, as such, it reflects another special feature of the general equation of motion that remains to be discovered. We finally introduce the entropy balance which is another powerful tool for analyses of physical phenomena.

At this stage of our exposition, energy and entropy are fully and rigorously defined for equilibrium as well as other states. The concepts of temperature and heat have not yet been either defined or used. We emphasize this fact because it is a most distinguishing feature of the exposition of thermodynamics adopted in this book.

In Chapter 8 we focus our attention on stable equilibrium states. We show that at a stable equilibrium state the value of any property is fully and uniquely determined by the values of the energy, the amounts of constituents, and the parameters. This conclusion is known as the state principle. It is reached without any extraneous considerations, such as lack of information, difficulty associated with complicated calculations, unpredictability of initial conditions, or lack of interest in making detailed analyses of large systems.

Next, we derive the highest-entropy principle and the lowest-energy principle as useful criteria for stable equilibrium. In applications of the highest-entropy principle, a key role is played by the special form of the state principle known as the fundamental relation. It avers that the value of the entropy at a stable equilibrium state is uniquely determined by the values of the energy, the amounts of constituents, and the parameters. Again, this is a rigorous and general result, involving no approximation whatsoever.

In Chapters 9 to 11 we use the highest-entropy principle to investigate necessary conditions that must be satisfied for two systems to be in mutual stable equilibrium, that is, for the composite of the two systems to be in a stable equilibrium state. These investigations disclose the existence of properties that are defined only for stable equilibrium states, namely, temperature (Chapter 9), total potential of a constituent (Chapter 10), and pressure (Chapter 11). Each of these properties is defined in terms of a partial derivative of the fundamental relation and is readily measurable. More important, we show that necessary conditions for systems to be in mutual stable equilibrium are temperature equality, total potential equality for each constituent, and pressure equality. Each of these equalities provides the theoretical foundation for the measurement of the respective property.

In Chapter 9 we discuss a novel derivation of the absolute values of entropy. We discover that the smallest value of entropy is common to all systems, and that it corresponds to the entropy of all the states contemplated in mechanics. Because the smallest value of entropy is common to all systems, we assign to it the value zero and end up with absolute values of entropy that are all nonnegative. Moreover, we conclude that mechanics is the physics or thermodynamics of zero-entropy states.

In Chapter 9 we also investigate the question of the lowest value of temperature for given values of the amounts of constituents and parameters, and for systems with no upper bound to the value of the energy. We prove that it is nonnegative and obtains at the ground-energy stable equilibrium state. If we were using quantum-theoretical concepts, we could prove that the smallest temperature must be equal to zero. Because we do not use such concepts, we omit the proof and introduce the zero-temperature requirement as the third law of thermodynamics.

In Chapter 12 we introduce work and heat interactions. A work interaction is defined by the condition that its result be a net exchange of energy between the interacting systems involving no exchange of entropy. A heat interaction is defined by the condition that it be entirely distinguishable from work—no part of a heat interaction be mistakable as a work interaction. We prove that such an interaction exists, results in a net exchange of both energy and entropy, requires that the interacting systems be almost at the same temperature, and is such that the ratio of the amount of energy exchanged to the amount of entropy exchanged equals the almost common temperature of the interacting systems. We explain that a heat interaction is only a special case of interactions that are not work, and that we call nonwork.

We discuss the energy balance and the entropy balance for a system experiencing work and heat interactions only. The change in energy equals the sum of the work and the heat to the system. This result is just a very special consequence of the two laws of thermodynamics and hence cannot be called "the first law." The change in entropy equals the entropy supplied by the heat interaction plus the entropy generated spontaneously by irreversibility within the system. Also this result is just a very special consequence of the two laws of thermodynamics and hence cannot be called "the second law."

Work and heat are ingenious concepts. For given end states of a system, they allow the quantitative distinction between entropy generated by irreversibility and entropy exchanged via interactions with other systems. As such, these two concepts provide practical means for identifying opportunities to reduce the entropy generation by irreversibility and hence to improve the performance of the system. The identification of these opportunities would be missed if the definition of heat were, for example, just any interaction that is not work, that is, any nonwork interaction.

In Chapter 13 a novel graph of energy versus entropy is introduced. It is used repeatedly to provide pictorial illustrations for most of the ideas discussed in Chapters 2 to 12. The illustrations include the zero-entropy lines that correspond to all states encountered in mechanics; projections of the multidimensional space of all types of states; the zero-temperature states specified by the third law; the fundamental relations that account for all states encountered in classical thermodynamics; the concepts of temperature, adiabatic availability, available energy, and irreversibility; and the effects of work, heat, and nonwork interactions. In addition, energy versus entropy diagrams are used in discussions of the role of the second law on the ground-energy zero-temperature stable equilibrium states, and of systems with energy that cannot be increased indefinitely. It is shown that some of the stable equilibrium states of the latter systems have negative temperatures.

Chapter 14, the beginning chapter for the undergraduate student, is a concise but precise summary of the foundations, that is, of the concepts, principles, and results discussed in Chapters 2 to 13. The summary is especially suited for engineering students who must get on with the job of applying the theory to practical problems. It deemphasizes the intellectual subtleties, complexities, and generalities of the subject, while providing the assurance that thermodynamics is a well-founded, well-reasoned, unambiguous, and consistent science with many triumphs and yet new horizons to conquer. It provides the material for two or three introductory lectures in a first undergraduate course on thermodynamics. The practical meaning of the various definitions is gradually grasped from their applications in subsequent chapters and problem solving.

In Chapter 15 we illustrate the point that the energy balance and the entropy balance are two of the most valuable tools for analyses of practical problems by applying these balances to heat engines, heat pumps, and refrigeration units. The remaining chapters address applications to specific systems and specific classes of states.

In Chapter 16 we begin with a general study of the properties of substances in stable equilibrium states by focusing on systems with external forces that are characterized by a single parameter, volume. We introduce many stable equilibrium state properties, such as enthalpy, Helmholtz free energy, Gibbs free energy, and heat capacities, and derive many relations between them, such as the Gibbs relation and the Maxwell relations. For various processes that involve only heat and work interactions and in which the system starts in a stable equilibrium state and ends in a neighboring stable equilibrium state, we discuss the relations between heat, work, temperature of the initial state, temperature at which the heat interaction occurs, pressure, changes in energy, entropy, and volume, and entropy generated by irreversibility.

In Chapter 17 we discuss simple systems. We define a system as simple if it has volume as the only parameter and if it can be partitioned into a set of contiguous subsystems in mutual stable equilibrium so that the effects of the partitioning are negligible. The condition on partitioning is very important because it allows the extension of properties of a given amount to both smaller and larger amounts. It is satisfied only if the values of the amounts of constituents are sufficiently large, say, larger than 10 molecules or atoms per type. We derive the Euler relation and the Gibbs–Duhem relation. We introduce the concepts of extensive, intensive, partial, and specific properties, and establish the number of independent variables required for the specification of each of these properties. All these concepts provide the theoretical framework for the study of properties of a substance in stable equilibrium states.

In Chapter 18 we define homogeneous and heterogeneous states and the concept of phase. Then we examine the question: Starting from an initial stable equilibrium state consisting of several coexisting phases, how many of the intensive properties temperature, pressure, and chemical potentials can be varied independently while the system changes to another stable equilibrium state consisting of the same types of phases as the initial state? We derive the answer, the so-called Gibbs phase rule.

In Chapter 19 we discuss the stable-equilibrium-state properties of pure substances modeled as simple systems. Experimental results on energy, enthalpy, and other properties are reported in graphical and tabular forms. Much is extracted from the experimental data on a given substance by combining them with the wealth of theoretical implications that follow from the state principle, in general, and the patterns of coexisting phases, in particular.

In Chapter 20 we consider certain limited ranges of temperature and pressure in which the relation between temperature, pressure, and volume, the so-called equation of state, takes a simple and explicit mathematical form. Under such conditions, which we call ideal-behavior conditions, properties are much easier to study because they can be described by simple analytical forms rather than by charts and tabulated data. Thus we describe the ideal-gas behavior and the many analytical interrelations that apply under such ideal behavior. We also describe the ideal-incompressible fluid or ideal-solid behavior.

In Chapter 21 we discuss some of the historical equations of state that have been developed to model the behavior of substances outside the ranges of validity of the ideal-gas behavior.

In Chapter 22 we define a special class of nonequilibrium states that we call bulk-flow states. We introduce another type of nonwork interaction, the bulk-flow interaction. It involves bulk-flow states and accomplishes transfers of energy, entropy, and amounts of constituents. Bulk-flow states and bulk-flow interactions play a major role in modeling energy-processing devices, energy-conversion systems, chemical reactors, and materials-processing systems.

In Chapter 23 we consider a number of simplified models of energy-conversion devices, such as nozzles, compressors, pumps, turbines, and heat exchangers. For each of these devices, we derive interrelations between end states, bulk-flow states of inlet and outlet streams, energy and entropy transfers, entropy generated by irreversibility, and empirical characteristics of the device.

In Chapter 24 we develop the concept of optimum work in processes experienced by a composite of a system and the environmental reservoir. We discuss generalizations of the concepts of adiabatic availability and available energy that apply to various combinations of conditions. Rather than building up the vocabulary, we call each such generalization an availability or exergy. We conclude the chapter with a discussion of a thermodynamic measure of efficiency, the ratio of the availability required by a change of state of a system to the availability consumed to effect this change.

In Chapter 25 we briefly discuss energy-conversion systems, external combustion and internal combustion engines, nuclear fission reactors, and hydropower plants. Then we review the typical energy-conversion systems following the traditional classification based on the historical working-fluid cycles. Excluded from these discussions are combustion phenomena, which are covered in Chapter 31.

In Chapter 26 we discuss the stable-equilibrium-state properties of mixtures modeled as simple systems. Experimental results on energy, enthalpy, and other properties are reported in graphical and tabular forms. As for pure substances, much can be extracted from the experimental data by combining them with the wealth of theoretical implications that follow from the state principle, in general, and the patterns of coexisting phases, in particular. The main objective here is to relate properties of a mixture to properties of the pure constituents. We show that this can be done via the concepts of partial pressure and equality of chemical potentials of systems in mutual stable equilibrium.

In Chapter 27 we consider certain limited ranges of temperature and pressure in which the relations between properties of a mixture and properties of pure constituents take simple and explicit mathematical forms. Under such conditions, which we call ideal-behavior conditions, properties are much easier to study because they can be described by simple analytical forms rather than through the use of charts and tabulated data. Thus we describe the ideal Gibbs–Dalton behavior, the ideal-gas mixture behavior, and the many analytical interrelations that apply under such ideal behaviors. As a typical engineering example, we discuss moist air, the mixture of air and water vapor. We also describe the ideal-solution behavior and the rudiments of two-phase mixture behavior such as needed to design distillation columns.

In Chapter 28 we discuss some of the historical relations between temperature, pressure, chemical potentials, and mole fractions that have been developed to model the behavior of substances outside the ranges of validity of the ideal-gas mixture and the ideal-solution behaviors.

Up to this point in the book we have not considered the effects of chemical reactions. In Chapters 29 and 30 we define the concepts and terminology that are needed for a description of simple systems subject to chemical reactions, present a novel derivation of the necessary conditions for chemical equilibrium, and evaluate the effects of chemical reactions on the stable-equilibrium-state properties.

In Chapter 31 we consider the special class of chemical reactions that correspond to the combustion or oxidation of fuels, namely the reactions that represent about 90% of the energy sources we use in energy-conversion devices.

Paradoxically, our experience shows that the study of this book is easier for a reader without much background in thermodynamics than for one who has been exposed to the traditional presentation and its statistical interpretation. The inexperienced student finds here a complete, logically consistent, and self-sufficient exposition. All concepts are defined carefully and explicitly so that the learning proceeds smoothly from the foundations to the applications. No previous knowledge of the subject is needed, except for a sophomore background in calculus and introductory physics.

Experienced readers may have some difficulty. They may be appalled when they read that thermodynamics applies equally well to macroscopic and microscopic phenomena, that entropy is equally defined for equilibrium and nonequilibrium states, and that temperature is meaningful and useful also for the stable equilibrium states of a single particle. Their dismay will persist unless they realize that the new perspective requires an intellectual reorientation and a subtle and demanding reconsideration of basic premises and concepts.

For us, the need for such reconsideration of premises and concepts has not arisen only from our didactic experience. It is stimulated by the results of research on the quantum foundations of physics performed by colleagues and ourselves. The results are published in the scientific literature. However, there is no need at all to be acquainted with either such literature or with the ideas of quantum theory in order to study any part of this book. We mention these results here only to assure our doubting reader that the advanced foundations of quantum physics lurk behind our exposition, and that each of the concepts we introduce has a sound counterpart in the most advanced formulation of contemporary physics.

Even the traditional meaning of the term thermodynamics needs to be reconsidered. Physics is the science that attempts to describe all aspects of all phenomena pertaining to the perceivable universe. It can be viewed as a large tree with many branches, such as mechanics, electromagnetism, gravitation, and chemistry, each specialized in the description of a particular class of phenomena. Thermodynamics is not a branch. It pervades the entire tree. To emphasize this conception, we often use the words physics and thermodynamics as synonyms.

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