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The Fundamentals of Thermodynamics

Springer

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It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of physics. There is something more palpably verbal about them—they smell more of their human origins. The guiding motif is strange to most of physics; namely, a capitalizing of the universal failure of human beings to construct perpetual motion machines of either the first or the second kind. Why should we expect nature to be interested either positively or negatively in the purposes of human beings, particularly purposes of such unblushingly economic tinge? (Bridgman, 1943, p. 3)

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore. (This reply (circa 1950) by Arnold Sommerfeld, when asked why he had never written a book on thermodynamics, given that he had written books on many other topics in physics, is *quoted in many places, for example, Fink (2009, p. 1).)*

The history of thermodynamics has always seemed to me to be not only one of the most interesting but one of the most dramatic episodes to be found in the story of the intellectual progress of the human mind. Starting in an investigation of a purely practical problem of engineering economics, it has grown into a body of doctrine of profound philosophical significance, …
(Wheeler, 1951, p. 64)

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.
(Einstein, 1979, p. 31)

Preface

In broad terms, thermodynamics is the branch of physics that is concerned with the macroscopic properties of matter in so far as they are related to heat, work, energy, temperature and entropy. These quantities are related to each other, and governed by fundamental laws. The First Law asserts the existence of the energy of a system: it is essentially a generalization of the mechanical principle of the conservation of energy. The Second Law, which is probably the most quoted (and sometimes misquoted) law of physics,[1] constrains the class of allowed processes between thermodynamic states and leads to the derivation of entropy and thence to temperature. To these laws, which originate in the nineteenth century, was added the Zeroth Law in the early twentieth century, which asserts the transitivity of the relationship of *being in equilibrium with* and leads to an independent definition of temperature without reference to entropy.[2] Finally, the early twenty-first century saw the introduction of the Minus First Law, asserting the evolution of systems towards equilibrium; this is discussed in more detail below.

Thermodynamics has been immensely fruitful, providing a vast number of successful predictions about systems as different as steam engines and black holes. Indeed, the theory is so successful that Einstein praised it as the only physical theory of universal content of which he was convinced that it would never be overthrown in its domain of application (quoted in the epigraph). Yet, when we turn to the foundations of the theory, enthusiasm quickly wanes. In the epigraph we have quoted notable physicists wondering about the nature of the exact articulation of the theory and worrying about its exact formulation. This scepticism is not limited to those, like Sommerfeld, who eventually decided to avoid the topic. Reiss (1965, p. vii)

[1] C. P. Snow (1959) famously argued in his lecture on the two cultures that the ability to state the Second Law was culturally on a par with having read a work of Shakespeare.

[2] The early twentieth century also saw the introduction of the so-called Third Law, which, in one of its forms, asserts the impossibility of reaching absolute zero temperature by a finite number of thermodynamic processes. This law plays no part in our discussion, and its status as part of the fundamental theory of thermodynamics remains contentious.

lists as one of the motivations for writing his now canonical textbook on thermodynamics “the almost certain truth that nobody (authors included) understands thermodynamics perfectly. The writing of a book therefore becomes a kind of catharsis in which the author exorcises his own demon of non-comprehension and prevents it from occupying the soul of another”.

In response to this situation, two families of approaches have emerged in the foundational literature on thermodynamics. Geometric approaches represent thermodynamic processes as curves in a state space and formulate the theory’s laws in terms of the relationships between curves of different types. Algebraic approaches represent process as operations on the system leading to ‘jumps’ from an initial state to a final state, without implying that the system passes through a curve of states between them. The possibility, and very importantly the impossibility, of processes between states is then formalized in terms of sets of axioms. The main aim of this book is to explore and develop the algebraic approach, although we have, by way of comparison, included a chapter containing a briefer account of the geometric approach (and it should be said that some material, particularly the discussion of critical phenomena is not tied to either approach). This project is not born out of the conviction that algebraic approaches are necessarily superior. Rather, it is motivated by the observation that algebraic approaches seem to have attracted less attention than their geometric alternatives. It is also the case that algebraic approaches, lend themselves well to the kind of axiomatization which lays bare the logical progression which, starting with first principles, allows the step-by-step building of the theory, without omissions or gaps. As we shall see, this is true for the work of Lieb and Yngvason, which is the inspiration for our approach.

After an introduction, we start by defining the state space of thermodynamic variables and thermodynamic processes, which are encapsulated in the concept of accessibility, whose algebraic properties are formulated in the first set of axioms. The main focus in thermodynamics is not on processes in general, but on a restricted class of adiabatic processes. Defining these leads to the First Law of which a consequence is the existence of the internal energy function, which can be identified as the thermal variable of the system. Two further sets of axioms follow. The first specializes accessibility to adiabatic process and the second defines a set of properties of what are called simple systems. An important consequence of these axioms taken together is that Carathéodory’s version of the Second Law can be derived as a *theorem*. It is crucial to note that neither temperature nor entropy has been introduced at this point and that the Second Law (and the restrictions that it imposes on allowable processes) can be understood, and explicitly formulated, without either of these notions. We then continue the development by introducing the final set of axioms, the Thermal Axioms. Although these encompass the idea of systems being in mutual thermal equilibrium, this can still be done without introducing temperature, which is defined only after we define entropy. Once both entropy and temperature are in place we can then compare the different versions of the Second Law: that due to Carathéodory and the conventional formulations due to Clausius, Kelvin and Planck.

This concludes our discussion of the algebraic approach. To pave the ground for a comparison with the alternative geometrical approach, we proceed to consider a more geometric approach based mainly on the development by Boyling of the work of Carathéodory leading to a view of thermodynamics from the perspective of contact geometry. The last two chapters of the book extend the scope of the discussion to, respectively, critical phenomena and non-equilibrium systems. The book is completed with a sequence of appendices. The discussion is advanced using sets of interlinked propositions, some of which require proofs which are provided in an Appendix. In addition the argument requires a number of interjections some of which are related to the relationship between thermodynamics and statistical mechanics. A more detailed description of this structure, together with two flow diagrams, is provided at the end of Chap. 1 in Sect. 1.4.

This book is in the first instance intended for physicists and mathematicians who work on the foundations of thermodynamics. We hope that it is also useful for philosophers of physics with a special interest in thermodynamics, as well as for practitioners who are curious about foundational questions. Familiarity with thermodynamics, as it is taught in advanced undergraduate or master's level courses[3] is presupposed, but not familiarity with the foundational literature on the subject.

Discussions that ultimately led to this book project started in the regular meetings of the Sigma Club at LSE, which both authors have been attending regularly for the last twenty odd years. We would like to thank the Sigma Club for making such exchanges possible, and for providing a platform where those interested in the philosophy of physics can meet and engage in conversation. We would also like to thank Elliott Lieb and Jakob Yngvason for encouraging us in the writing of this book, and Reimer Kühn for many helpful discussions. We are also grateful to Angela Lahee and Lisa Scalone, and the staff at Springer, for their work in the production of the book. Last but not least, we would like to thank our families and partners for their unwavering support throughout the process of writing.

The translations from German and French which appear as footnotes in the text are our own.

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[3] Buchdahl (1966), Fermi (1937), Pippard (1961), Reiss (1965), ter Haar and Wergeland (1966) and Zemansky (1968) are advanced courses of the kind we have in mind.

Contents