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Michele Campisi

Lectures on the Mechanical Foundations of Thermodynamics

Second Edition

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To Elisa,
my life.
To the memory of Prof. Donald H. Kobe,
mentor and example.

Foreword

Thermodynamics, conceived more than 150 years ago by Carnot, Clausius, and others, has been experiencing a remarkable resurgence over the last two decades, spurred by major experimental and technological advances that enable the direct observation and manipulation of quantum gases, DNA molecules, and other nanoscale systems. Originally developed to describe heat exchange and work extraction processes at the macroscopic scales, it has become increasingly clear in recent years that thermodynamic concepts and principles provide an equally powerful framework for the theoretical description of energy and information transfer in microscopic systems, from quantum heat engines to biological cells. Michele Campisi, whom I first met while still a doctoral student in Peter Hänggi's group at Augsburg, has been one of the pioneers at the forefront of this rapidly expanding research field.

In his monograph *Lectures on the Mechanical Foundations of Thermodynamics*, which is based on courses he taught at the University of Florence, Michele discusses how a thermodynamic framework can be systematically constructed from Hamiltonian dynamics. This fundamental question has a long and interesting history, dating back to seminal work by Boltzmann, Gibbs, and Hertz at the turn of the twentieth century, and it has regained critical importance with recent applications of thermostatistical concepts to small systems. While many modern textbooks adopt an axiomatic approach that starts from an abstract set of thermodynamic postulates, the constructive "bottom-up" approach pursued in this monograph shows how a reduced thermodynamic description emerges naturally by linking dynamical time averages with statistical ensemble averages through the ergodicity hypothesis.

Rather than aiming for a broad scope of applications, Michele's lectures focus on building a deep and succinct understanding of thermostatistical core concepts. Carefully chosen pedagogical examples highlight the different physical assumptions underlying the microcanonical and canonical ensembles. Ensemble equivalence, often taken for granted in the thermodynamic limit, can be and is violated in small (and many not-so-small) systems, which has profound implications for the accurate description of energy conversion and transfer in microbiological and quantum processes. Students and researchers interested in developing a strong foundational understanding of thermodynamic concepts will greatly appreciate the guidance provided by this monograph.

Over the last 15-plus years, I have learned immensely from my many discussions with Michele, as well as from studying his original research papers and review articles—after reading his monograph, you will surely feel the same way.

Cambridge, MA, USA
August 2021

Jörn Dunkel

Preface

The largest majority of textbooks presents the subject of statistical mechanics by adding one or more postulates to the microscopic theory that describes the dynamics of the constituents of matter, be it classical mechanics or quantum mechanics. Typically, one postulates the entropy and then derives thermodynamics therefrom. However, that is not desirable from a foundational point of view, because when adding a postulate to an existing theory, there is always a risk that it is not fully coherent with it.

The present series of lectures provides an introduction to statistical mechanics, specifically the theory of statistical ensembles, that does not require any further postulate besides the laws that govern the Hamiltonian (classical) dynamics of the constituents of macroscopic bodies. Rather it requires an assumption: the ergodic hypothesis. The approach adopted here can be traced back to the early works of Boltzmann [1], following an underground line (mostly unknown to the modern readers) that has received important later contributions by Helmholtz [2, 3], Boltzmann himself [4], Gibbs [5], P. Hertz [6], and Einstein [7]. I tried to present the material in an original and organic manner, casted in modern language and notation, and integrated with basic ergodic theory (as presented, e.g., in the textbook of Khinchin [8]), avoiding as much as possible unnecessary mathematical abstraction and complications.

The material presented is rather limited in comparison to what is customarily taught in a graduate course of statistical mechanics. It is meant only to cover the foundations of statistical ensembles and can be used as the first set of lectures of a complete course. It constitutes an ideal continuation of a graduate course in classical mechanics. Knowledge of basic calculus in many dimensions (including differential forms), thermodynamics, basic probability theory, and Hamiltonian mechanics are prerequisites for these lectures. Special attention is devoted to the Massieu potentials (the Legendre transforms of the entropy) which are most natural in statistical mechanics and also allow for a more direct treatment of the topic of ensemble equivalence. A number of exercises are scattered through the text, to stimulate learning and understanding. Many derivations, due to their simplicity, are skipped and proposed as exercises.

An important remark is in order for the teacher who wishes to use these lectures in a course of statistical mechanics. The theory presented here leads univocally to identify the thermodynamic entropy of an isolated system as the logarithm of the Liouville measure of the region of phase space enclosed by the energy hyper-surface, which is often referred to as volume entropy. That is in contrast with the standard textbook approach that postulates entropy as the logarithm of the invariant measure of said hyper-surface (the surface entropy), or, for the discrete system, the logarithm of the number of microstates according to Boltzmann's famous formula $S = k \ln W$. The latter formula is customarily used to treat various classic topics in the statistical mechanics of discrete systems (for example, when discussing the absence of phase transitions in the 1D Ising model, i.e., the argument of Landau and Peierls) which poses the question of how they should be treated within the present approach. In my experience, the formula $S = k \ln W$ could always be avoided, and that typically helped in improving the clarity. For example, the Landau and Peierls argument can be consistently presented as an application of the variational principle according to which the functional $f[\rho] = \mathrm{Tr} H\rho + T \mathrm{Tr} \rho \ln \rho$ is always larger or equal than the thermodynamic free energy F that is attained by the equilibrium canonical distribution $\rho \propto e^{-\beta H}$. The argument goes smoothly in this way and avoids the questionable habit, that permeates the whole literature, of calling non-equilibrium quantities, such as f or $-\mathrm{Tr} \rho \ln \rho$, with the name of thermodynamic potentials (free energy and entropy, respectively), which instead are, by definition, equilibrium quantities.

Chapter 1 is a quick review of the central statements of thermodynamics; the Massieu and standard potentials are introduced here. Chapter 2 presents the most minimal mechanical model of a thermodynamic system, namely a single particle in a 1D box. Thanks to the Helmholtz theorem that helps in realising that the thermodynamic structure is implicit in Hamiltonian mechanics. The chapter serves as an introduction to the ergodic theory, the microcanonical ensemble, and the generalised Helmholtz theorem, which are the subject of Chap. 3. Chapter 4 is devoted to the canonical ensemble, which is presented as the statistics that describes a system in weak contact with a large ideal gas. Chapter 5 deals with releasing the constraint on volume and presents *TP*-ensemble as the ensemble that emerges from the canonical ensemble when the position of a movable piston is raised to the rank of a dynamical variable. Chapter 6 deals with the release of the constraint on the number of particles, namely, the grand-canonical ensemble. At variance with the standard textbook presentation, it is presented as an almost direct consequence of an assumption of "complete randomness" of the statistics of particle number (i.e., its Poissonian character is assumed), which is often implicit in standard derivations. Finally, Chap. 7 discusses the topic of ensemble equivalence, following a personal approach influenced by the works of Ruffo and others [9]. For all ensembles presented, their statistical-dynamical origin is highlighted, and thermodynamics is, according to the early Boltzmann spirit, never used as an input for their construction, rather it is presented as an aftermath.

The material is based on lectures delivered at the University of Florence in the academic years 2019/2020 and 2020/2021 as part of the course of Statistical Mechanics.

This second edition features some minor amendments and embellishments, and the addition of a chapter (Chap. 8) that deals with the question about what happens to the mechanical expression of entropy when Hamiltonian systems are driven away from equilibrium by means of a non-adiabatic forcing. It is shown that provided the system is initially in a so called passive state (e.g., the thermal equilibrium state) such entropy can only increase. Concentration of measure ensures that this happens as well when the system is initially in any stationary state, in the thermodynamic limit. This addition was necessary to provide a complete and coherent understanding of the second law within the mechanical approach to the foundations of thermodynamics. Furthermore the newly added Chap. 8 presents an excellent starting point for introducing some central concepts in the modern theory of quantum thermodynamics, such as "passivity" and "ergotropy". The material in Chap. 8 is based on lectures delivered at the University of Pisa in the academic year 2023/2024.

Pisa, Italy
November 2024

Michele Campisi

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