Thermal Physics: Concepts and Practice

Thermodynamics has benefited from nearly 100 years of parallel development with quantum mechanics. As a result, thermal physics has been considerably enriched in concepts, technique and purpose, and now has a dominant role in developments of physics, chemistry and biology. This unique book explores the meaning and application of these developments using quantum theory as the starting point.

The book links thermal physics and quantum mechanics in a natural way. Concepts are combined with interesting examples, and entire chapters are dedicated to applying the principles to familiar, practical and unusual situations. Together with end-of-chapter exercises, this book gives advanced undergraduate and graduate students a modern perception and appreciation for this remarkable subject.

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Thermal Physics

Concepts and Practice

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Preface

In the preface to his book Statistical Mechanics Made Simple Professor Daniel Mattis writes:

> My own experience in thermodynamics and statistical mechanics, a half century ago at M.I.T., consisted of a single semester of Sears, skillfully taught by the man himself. But it was a subject that seemed as distant from "real" physics as did poetry or French literature.[1]

This frank but discouraging admission suggests that thermodynamics may not be a course eagerly anticipated by many students – not even physics, chemistry or engineering majors – and at completion I would suppose that few are likely to claim it was an especially inspiring experience. With such open aversion, the often disappointing performance on GRE[2] questions covering the subject should not be a surprise. As a teacher of the subject I have often conjectured on reasons for this lack of enthusiasm.

Apart from its subtlety and perceived difficulty, which are probably immutable, I venture to guess that one problem might be that most curricula resemble the thermodynamics of nearly a century ago.

Another might be that, unlike other areas of physics with their epigrammatic equations – Newton's, Maxwell's or Schrödinger's, which provide accessibility and direction – thermal physics seems to lack a comparable unifying principle.[3] Students may therefore fail to see conceptual or methodological coherence and experience confusion instead.

With those assumptions I propose in this book alternatives which try to address the disappointing experience of Professor Mattis and undoubtedly others.

Thermodynamics, the set of rules and constraints governing interconversion and dissipation of energy in macroscopic systems, can be regarded as having begun with Carnot's (1824) pioneering paper on heat-engine efficiency. It was the time of the industrial revolution, when the caloric fluid theory of heat was just being questioned and steam-engine efficiency was, understandably, an essential preoccupation. Later in that formative period Rudolf Clausius introduced a *First Law of Thermodynamics* (1850), formalizing the principles governing macroscopic energy conservation.

1 Daniel Mattis, *Statistical Mechanics Made Simple*, World Scientific Publishing, Singapore (2003).
2 Graduate Record Examination: standardized graduate school admission exam.
3 R. Baierlein, "A central organizing principle for statistical and thermal physics?", *Am. J. Phys*. **63**, 108 (1995).

Microscopic models were, at the time, largely ignored and even regarded with suspicion, to the point where scientific contributions by some proponents of such interpretations were roundly rejected by the editors of esteemed journals. Even with the intercession in support of kinetic models by the respected Clausius (1857), they stubbornly remained regarded as over-imaginative, unnecessary appeals to invisible, unverifiable detail – even by physicists. A decade later when Maxwell (1866) introduced probability into physics bringing a measure of statistical rigor to kinetic (atomic) gas models there came, at last, a modicum of acceptance.

Within that defining decade the already esteemed Clausius (1864) invented a novel, abstract quantity as the centerpiece of a *Second Law of Thermodynamics*, a new principle – which he named *entropy* – to change forever our understanding of thermal processes and, indeed, all natural processes. Clausius offered no physical interpretation of entropy, leaving the matter open to intense speculation. Ludwig Boltzmann, soon to be a center of controversy, applied Maxwell's microscopic probability arguments to postulate a statistical model of entropy based on counting discrete "atomic" configurations referred to, both then and now, as "microstates".[4] However, Boltzmann's ideas on entropy, which assumed an atomic and molecular reality, were far from universally embraced – a personal disappointment which some speculate led to his suicide in 1906.

Closing the book on 19th-century thermal physics, J. W. Gibbs reconciled Newtonian mechanics with thermodynamics by inventing *statistical mechanics*[5] based on the still mistrusted presumption that atoms and molecules were physical realities. In this indisputably classic work, novel statistical "ensembles" were postulated to define thermodynamic averages, a statistical notion later adopted in interpreting quantum theories. Shortcomings and limited applicability of this essentially Newtonian approach notwithstanding, it provided prescient insights into the *quantum mechanics*, whose full realization was still a quarter century in the future.

Quantum mechanics revolutionized physics and defines the modern scientific era. Developing in parallel with it, and synergistically benefiting from this reshaped scientific landscape, thermal physics has come to occupy a rightful place among the pillars of modern physics.

Quantum mechanics' natural, internally consistent unification of statistics with microscopic mechanics immediately suggests the possibility of a thermodynamics derived, in some way, from microscopic quantum averages and quantum probabilities. But thermodynamic systems are not simply the isolated quantum systems familiar from most quantum mechanics courses. Thermodynamics is about *macroscopic* systems, i.e. many-particle quantum systems that are never perfectly isolated from the remainder of the universe. This interaction with the "outside" has enormous

4 Boltzmann's microstates suggested to Planck (1900) what eventually became the quantization he incorporated into his theory of electromagnetic radiation.
5 J. W. Gibbs, *The Elementary Principles of Statistical Mechanics*, C. Scribner, New York (1902).

consequences which, when taken into account quantitatively, clarifies the essence of thermodynamics.

Many thermal variables may then be approached as macroscopic quantum averages and their associated thermal probabilities as macroscopic quantum probabilities, the micro-to-macro translation achieved in part by an entropy postulate. This approach gives rise to a practical organizing principle with a clear pedagogical path by which thermodynamics' structure attains the epigrammatic status of "real physics".

Thermal physics is nevertheless frequently taught in the spirit of its utile 19th-century origins, minimizing both 20th- and 21st-century developments and, for the most part, disregarding the beauty, subtlety, profundity and laboratory realities of its modern rebirth – returning us to Professor Mattis' reflections. In proposing a remedy for his justifiable concerns, the opening chapter introduces a moderate dose of quantum-based content, both for review and, hopefully, to inspire interest in and, eventually, better understanding of thermodynamics. The second chapter develops ideas that take us to the threshold of a thermodynamics that we should begin to recognize. In Chapter 6 thermodynamics flies from a quantum nest nurtured, ready to take on challenges of modern physics.

Students and practitioners of thermodynamics come from a variety of disciplines. Engineers, chemists, biologists and physicists all use thermodynamics, each with practical or scientific concerns that motivate different emphases, stress different legacies and demand different pedagogical objectives. Since contemporary university curricula in most of these disciplines integrate some modern physics, i.e. quantum mechanics – if not its mathematical details at least its primary concepts and aims – the basic thermodynamic ideas as discussed in the first two chapters should lie within the range of students of science, engineering and chemistry. After a few chapters of re-acquaintance with classic thermodynamic ideas, the book's remaining chapters are dedicated to applications of thermodynamic ideas developed in Chapter 6 in practical and model examples for students and other readers.

Parts of this book first appeared in 1997 as notes for a course in thermal physics designed as a component of the revised undergraduate physics curriculum at Oregon State University. An objective of this revision was to create paradigmatic material stressing ideas common to modern understandings and contemporary problems. Consequently, concepts and dynamic structures basic to quantum mechanics – such as hamiltonians, eigen-energies and quantum degeneracy – appear and play important roles in this view of thermal physics. They are used to maintain the intended "paradigm" spirit by avoiding the isolation of thermal physics from developments of the past 100 years while, hopefully, cultivating in students and teachers alike a new perception of and appreciation for this absolutely remarkable subject.

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