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continued after Index

David R. Owen

A First Course in the Mathematical Foundations of Thermodynamics

With 52 Illustrations

Springer-Verlag
New York Berlin Heidelberg Tokyo

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AMS Subject Classification: 80-01

Library of Congress Cataloging in Publication Data
Owen, David R.
A first course in the mathematical foundations of thermodynamics.
(Undergraduate texts in mathematics)
Bibliography: p.
Includes index.
1. Thermodynamics. 2. Thermodynamics—Mathematics.
I. Title. II. Series.
QC311.094 1983 536′.7 83-14705

Softcover reprint of the hardcover 1st edition 1984

Typeset by Science Typographers, Medford, New York.

9 8 7 6 5 4 3 2 1
ISBN-13: 978-1-4613-9507-2 e-ISBN-13: 978-1-4613-9505-8
DOI: 10.1007/978-1-4613-9505-8

To Diane, Danny, Mom, and Dad

Preface

Research in the past thirty years on the foundations of thermodynamics has led not only to a better understanding of the early developments of the subject but also to formulations of the First and Second Laws that permit both a rigorous analysis of the consequences of these laws and a substantial broadening of the class of systems to which the laws can fruitfully be applied. Moreover, modern formulations of the laws of thermodynamics have now achieved logically parallel forms at a level accessible to undergraduate students in science and engineering who have completed the standard calculus sequence and who wish to understand the role which mathematics can play in scientific inquiry.

My goal in writing this book is to make some of the modern developments in thermodyamics available to readers with the background and orientation just mentioned and to present this material in the form of a text suitable for a one-semester junior-level course. Most of this presentation is taken from notes that I assembled while teaching such a course on two occasions. I found that, aside from a brief review of line integrals and exact differentials in two dimensions and a short discussion of *infima* and *suprema* of sets of real numbers, juniors (and even some mature sophomores) had sufficient mathematical background to handle the subject matter. Many of the students whom I taught had very limited experience with formal and rigorous mathematical exposition. For this reason, I have begun with a presentation of the foundations of classical thermodynamics in which many aspects of modern treatments are introduced in the concrete and simple setting of homogeneous fluid bodies. In addition, this material gives the student enough background to permit independent study of the vast classical literature and provides for an appreciation of the historical roots and logical structure of the modern treatments. I have benefited greatly from the beautiful exposition of classical thermodynamics by Truesdell and Bharatha[1], and my presentation of classical thermodynamics follows theirs in many respects. Because the main part of this book is itself an extension and broadening of the classical subject, I have chosen to give only an elementary, direct account of the classical foundations. In particular, I have treated a very limited subclass of the homogeneous fluid bodies covered by Truesdell and Bharatha.

Chapters II through V contain the basic material on the modern foundations of thermodynamics in the form of parallel treatments of the First and Second Laws. The laws of thermodynamics are first stated in terms of the concepts of heat, hotness, and work and mention only *special cycles* of a thermodynamical system. The main goal in these chapters is to express the content of these laws in terms of *arbitrary processes* of a system. This turns out to be more difficult in the case of the Second Law, because it is a non-trivial matter even to re-express its content in a form which applies to arbitrary cycles. The results of Chapters III and IV establish the equivalence of the First and Second Laws with statements of the following type: *a distinguished interaction between a system and its environment either vanishes or is of fixed sign in every cycle*. For the First Law, this statement expresses the fact that thermal and mechanical interactions are comparable in a simple and precise sense. For the Second Law, this statement is a generalization of the Clausius inequality given in traditional treatments of thermodynamics and, in rough terms, says that the integral of the heat added divided by absolute temperature is never positive for a cycle. It is important to note here that the notion of an absolute temperature scale emerges from the analysis leading to this equivalent statement of the Second Law and permits one to free the original statement of the Second Law from its restriction to special cycles. A similar remark applies to the notion of "the mechanical equivalent of heat" with respect to the First Law.

The main goal of the modern development is fully realized in Chapter V, where statements of the type in italics above are shown to be equivalent to the existence of functions of state whose differences are equal to or provide upper bounds for the distinguished interactions. In the case of the First Law, equality holds and the function of state is called an energy function for the system; for the Second Law, the function of state, or "upper potential", is called an entropy function. At bottom, the modern work on foundations shows that the concepts of absolute temperature, energy, and entropy can be obtained as consequences of primitive, natural, and general statements of the First and Second Laws, and such concepts yield equivalent statements of these laws which are known to be important for applications.

[1]Classical Thermodynamics as a Theory of Heat Engines, 1977, New York Heidelberg Berlin: Springer-Verlag.

As I mentioned above, the study of homogeneous fluid bodies in Chapter I helps to ease the reader into the more abstract and formal modern work, and homogeneous fluid bodies appear extensively in Chapters II through V both as illustrations and as important "model systems". Because modern applications include many systems not describable as homogeneous fluid bodies, I have devoted the bulk of Chapters VI and VII to a discussion of the main features of some important non-classical systems: viscous filaments, elastic–perfectly plastic filaments, and homogeneous bodies with viscosity. In order to keep the discussion at the right mathematical level and to permit easy comparison with the earlier analysis of homogeneous fluid bodies, I chose to maintain the classical assumption of spatial homogeneity. The additional restriction to isothermal processes made in Chapter VI provides further simplification: it yields a statement of the Second Law which mentions only the concept of work. In Chapter VI, elastic filaments are the counterparts of homogeneous fluid bodies, in that every process of an elastic filament has a reversal, and the work action changes signs under reversals. Viscous filaments do not have these properties, but instead exhibit approximate behavior of this type when processes are performed sufficiently slowly. Elastic–perfectly plastic filaments are similar to viscous filaments, in that they do not admit reversals of arbitrary processes. However, they differ from viscous filaments in an important way: there is no approximation for elastic–perfectly plastic behavior which yields a classical analysis of reversals.

I regard the study of systems with viscosity as crucial for a thorough understanding of thermodynamics, because these systems provide a simple and precise way of making explicit one of the kinds of approximations which underlie the concept of "quasi-static processes" in traditional presentations. Therefore, I have devoted a second section of Chapter VI as well as all of Chapter VII to systems with viscosity. In Section 4 of Chapter VI, I begin with the notion of the latent heat associated with a phase transition at fixed temperature in an elastic filament. Although the latent heat is not well defined for an analogous process in a viscous filament, it is natural to consider an elastic filament which approximates the viscous filament in slow processes and to compare its latent heat with the heat gained by the viscous filament. The results of this analysis give a vivid illustration of the lack of symmetry in the roles which thermal and mechanical energy play in nature: work done against viscous forces in a filament can contribute to melting or vaporization, but solidification and condensation cannot cause viscous forces in the filament to do work on its surroundings. In Chapter VII, I remove the restriction that processes be isothermal and study the consequences of the First and Second Laws for homogeneous viscous bodies. The modern conceptual framework is employed to analyze viscous bodies, and this analysis features homogeneous fluid bodies as approximating systems. The material in Chapter VII helps the reader to view the results of Chapter I on classical thermodynamics from a modern perspective and establishes the consistency of the classical and modern approaches.

The reader will notice that this book is not self-contained in two respects. First of all, I have not attempted to provide here the background material from elementary mathematical analysis used throughout the book. This material includes standard notions of continuity, differentiability, and integrability (in Riemann's sense) for real-valued functions of no more than three variables. Secondly, I have not discussed the background for the concepts of heat and hotness in a way which emphasizes the physical underpinnings of these notions. Such a discussion would fall under the headings of calorimetry and thermometry in standard physics texts on thermodynamics. For both types of background material, I have provided references at the end of this book. Also, I have there outlined the contributions of various researchers to modern thermodynamics and have provided references to some of their work. In the outline and references, no attempt has been made to survey all of the interesting and fruitful areas of modern research in thermodynamics. Indeed, attention is focused there on work closely related to the approach taken in this book. Nevertheless, some of the references given there will help the reader who is interested in other directions of modern research.

It is a pleasure to acknowledge the inspiration and encouragement provided through the years by my teachers and colleagues Bernard D. Coleman, Morton Gurtin, Walter Noll, James Serrin, and Clifford Truesdell. It is my hope that this book adequately reflects not only their specific contributions to thermodynamics but also a common goal underlying their scientific research: the realization of a harmonious union of natural science and mathematics. I wish also to thank John Thomas for his helpful comments at various stages in the preparation of this book and Stella DeVito for her expert typing of the manuscript. Finally, I am indebted to Ernest MacMillan and K. R. Rajagopal for their careful reading of the galleys and page proofs.

Contents

Introduction

Thermodynamics studies the mechanisms through which physical systems become hotter or colder. Such mechanisms include conduction of electricity, mechanical friction, thermal radiation, and surface heat transfer. One of the important tasks of thermodynamics is to explore the restrictions which nature places on these mechanisms. An example of a restriction of this type is obtained by considering a metal block at rest on a rough metal table with both block and table at the same temperature T_1. Our physical experience tells us that the two objects will not in and of themselves supply thermal energy to their common interface with the effect that the block accelerates from rest relative to the table, and the block and table both attain a lower temperature T_0. On the other hand, our experience does accept as plausible the reverse sequence of events: both objects begin at temperature T_0 with the block moving relative to the table and then the block decelerates to rest while the objects heat up to temperature T_1. This example suggests that relative motion of rough surfaces in contact can cause objects to become hotter, but that objects do not spontaneously cool down in order to initiate such relative motion. In other terms, the initial mechanical energy of the moving block can cause thermal energy to flow into the block and the table, whereas that same thermal energy of the rest system is not directly available for supplying mechanical energy to the block. Thus, mechanical and thermal energy appear not to play symmetrical roles in nature, and other elementary examples show this to be the case of electrical and thermal energy. The main goal of thermodynamics is to make such restrictions explicit and to analyze the consequences of these restrictions.

Much of classical thermodynamics concerns thermal and mechanical interactions between a physical system and its environment. In fact, when thermodynamics emerged in the last century as a science, there was much effort devoted to the problem of designing efficient engines which could deliver work through the heating and cooling of an operating medium such as water, and the celebrated Second Law of thermodynamics itself arose out of attempts to maximize the efficiency of heat engines. Throughout this presentation, thermal and mechanical interactions will be studied to the exclusion of electromagnetic and chemical interactions. Thus, we may call the subject of this book *thermomechanics* and content ourselves with the fact that a solid understanding of this subject will provide a basis for the study of other branches of thermodynamics.

The physical concepts underlying thermomechanics turn out to be those of heat, hotness and work, and these concepts are at the heart of both classical and modern treatments. Where classical and modern approaches to thermomechanics differ is in the nature of the physical systems which they attempt to study. One of the major aims of this book is that of making these differences explicit. For the moment it suffices to say only that modern treatments of thermomechanics cover a much broader class of physical systems than do the classical treatments.

The restrictions on interacting systems which form the basis of thermodynamics usually begin as observations about simple physical systems and are subsequently restated as general laws which are required to hold "universally." Much of the difficulty in traditional treatments of thermodynamics lies in a failure to make explicit the meaning of the word "universally." To give this word a clear meaning and thereby to delimit the scope of thermodynamics requires the use of a precise language to describe basic concepts, to state assumptions, and to carry out logical arguments. Mathematics is the most appropriate language for this purpose, and the reader will note from the outset that this presentation uses mathematics more extensively than most. Indeed, this presentation is axiomatic in nature, as are the standard presentations of Euclidean geometry. In order to prevent discussions from becoming unduly formal, I shall try to provide whenever possible physical motivation for the assumptions made and physical interpretations for the results obtained. Thus, my goal is to present some basic aspects of thermodynamics by allowing physical ideas to provide the basic input and mathematical structure to provide the vehicle for expressing and developing these ideas.

List of Symbols

$\mathscr{F}$	homogeneous fluid body	I-1
Σ	state space	I-1
V	volume	I-1
θ	temperature	I-1
$\mathscr{p}$	pressure function	I-1
$\tilde{\lambda}$	latent heat function	I-1
$\mathscr{c}$	specific heat function	I-1
$\mathbb{R}$	real numbers	I-1
$\mathbb{R}^{++}$	$(0, \infty) =$ positive real numbers	I-1
$\mathbb{P}$	path	I-1
$(\bar{V}, \bar{\theta})$	standard parameterization	I-1
$W(\mathbb{P})$	work done along $\mathbb{P}$	I-1
$H(\mathbb{P})$	net heat gained along $\mathbb{P}$	I-1
$\bar{\mathrm{h}}(\tau)$	heating at time τ	I-1
$H^{+}(\mathbb{P})$	heat absorbed along $\mathbb{P}$	I-1
$H^{-}(\mathbb{P})$	heat emitted along $\mathbb{P}$	I-1
$\mathbb{P}_r$	reversal of $\mathbb{P}$	I-1
$\mathbb{P}_2 * \mathbb{P}_1$	$\mathbb{P}_1$ followed by $\mathbb{P}_2$	I-1
$\mathrm{Int}\,\mathbb{P}$	interior of $\mathbb{P}$	I-1
$\mathrm{J}, \mathrm{R}, \lambda$	constants for an ideal gas	I-1
$\mathscr{G}$	ideal gas	I-1
E	energy function	I-2
J	mechanical equivalent of heat	I-2
$\check{W}$	work done on $\mathscr{F}$	I-2
$\mathbb{C}$	Carnot heat engine	I-3
S	entropy function	I-3

E°	normalized energy function	I-3
S°	normalized entropy function	I-3
Π	set of process generators	II-1
π	process generator	II-1
ρ_π	transformation induced by π	II-1
$\mathscr{D}(\pi)$	domain of ρ_π	II-1
$\mathscr{R}(\pi)$	range of ρ_π	II-1
$\Pi\sigma$	set of states accessible from σ	II-1
$\pi''\pi'$	π' followed by π''	II-1
$\varnothing$	empty set	II-1
$\rho_{\pi'}^{-1}$	inverse image function for $\rho_{\pi'}$	II-1
$\Pi\Diamond\Sigma$	set of processes of (Σ, Π)	II-1
$(\Sigma_{\mathscr{F}}, \Pi_{\mathscr{F}})$	system with perfect accessibility corresponding to a homogeneous fluid body $\mathscr{F}$	II-1
π_t	a process generator for $(\Sigma_{\mathscr{F}}, \Pi_{\mathscr{F}})$	II-1
$\Gamma(\pi_t, \sigma)$	path determined by (π_t, σ)	II-1
$(\Pi\Diamond\Sigma)_{\text{cyc}}$	the set of cycles of (Σ, Π)	II-1
a	an action	II-2
a_H	the action determined by the heat gained H	II-2
$\mathscr{S}$	thermodynamical system	III-1
$(\Sigma_{\mathscr{S}}, \Pi_{\mathscr{S}})$	system with perfect accessibility corresponding to a thermodynamical system $\mathscr{S}$	III-1
$W_{\mathscr{S}}$	work action for $\mathscr{S}$	III-1
$H_{\mathscr{S}}$	heat action for $\mathscr{S}$	III-1
$(\Pi_{\mathscr{S}}\Diamond\Sigma_{\mathscr{S}})_{\text{cyc}}$	the set of cycles of $\mathscr{S}$	III-1
$\mathscr{S}_1 \times \mathscr{S}_2$	product of $\mathscr{S}_1$ and $\mathscr{S}_2$	III-2
$\mathbb{U}$	a collection of systems	III-3
$\mathscr{M}$	hotness manifold	IV-2
$\prec$	order on hotness manifold	IV-2
L	hotness level	IV-2
$\mathscr{T}$	set of empirical temperature scales	IV-2
φ	empirical temperature scale	IV-2
$\varphi_{\mathscr{G}}$	empirical temperature scale for an ideal gas $\mathscr{G}$	IV-3
$H_{\mathscr{G}}$	accumulation function for an ideal gas $\mathscr{G}$ (as a function of hotness)	IV-3
$\hat{H}_{\mathscr{G}}$	accumulation function for an ideal gas $\mathscr{G}$ (as a function of temperature)	IV-3
$\mathbf{A}$	the adiabat in the proof of the Lemma	IV-3
$H_{\mathscr{S}}$	accumulation function for a thermodynamical system $\mathscr{S}$	IV-4
L′, L″	lower and upper hotness levels for a process	IV-4
$H_{\mathscr{S}}(\pi, \sigma, \mathrm{L})$	net heat gained by $\mathscr{S}$ in the process (π, σ) at or below L	IV-4
$H_{\mathscr{S}}(\pi, \sigma)$	net heat gained by $\mathscr{S}$ in the process (π, σ)	IV-4

$H_{\mathscr{S}}^{\downarrow}$	net heat absorbed	IV-7
$H_{\mathscr{S}}^{\uparrow}$	net heat emitted	IV-7
A	upper potential for an action	V-2
E	energy function	V-3
$\check{W}_{\mathscr{S}}$	work done on $\mathscr{S}$ by its environment	V-4
Ψ	Helmholtz free energy function	V-4
ℓ	length of a homogeneous filament	VI-1
f	external force on a filament	VI-1
(ℓ_a, ℓ_b)	interval of admissible lengths of a filament	VI-2
ϕ_e	response function of an elastic filament	VI-2
ω_e	work action for an elastic filament	VI-2
k	constant for a linear spring	VI-2
r	rate of change of length of a viscous filament	VI-3
ϕ_v	response function of a viscous filament	VI-3
ω_v	work action for a viscous filament	VI-3
$\mu(\ell)$	viscosity of a linear viscous filament	VI-3
$\tilde{\ell}_n$	retardation of a process of a filament	VI-3
ϕ_{eq}	equilibrium response function for a viscous filament	VI-3
Φ_{eq}	antiderivative of ϕ_{eq}	VI-3
Φ_v°	normalized Helmholtz free energy function of a viscous filament	VI-3
f_y	yield force of an elastic-plastic filament	VI-4
β	elastic modulus of an elastic-plastic filament	VI-4
ℓ_R	residual length	VI-4
ω_{ep}	work action for an elastic-plastic filament	VI-4
$\mathscr{L}^\circ$	the class of normalized Helmholtz free energy functions for an elastic-plastic filament	VI-4
$\hat{\Psi}^\circ, \Psi^\circ$	smallest and largest Helmholtz free energy functions	VI-4
$\hbar_e$	heat action for an elastic filament	VI-5
f_{tr}	force at which a phase transition occurs	VI-5
λ_{12}	latent heat	VI-5
$\hbar_v$	heat action for a viscous filament	VI-5
E_v	internal energy function of a viscous filament	VI-5
$\mathscr{V}$	homogeneous body with viscosity	VII-1
$\tilde{\mu}$	response function for a viscous body	VII-1
Γ_{eq}	equilibrium path	VII-1
$(\Sigma_{\mathscr{V}}, \Pi_{\mathscr{V}})$	system with perfect accessibility for a viscous body $\mathscr{V}$	VII-1
$W_{\mathscr{V}}$	work action for a viscous body	VII-1
$H_{\mathscr{V}}$	accumulation function for a viscous body	VII-1
$I_{\mathscr{V}}$	accumulation integral for a viscous body	VII-1