Thermodynamics

I Müller

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Foreword

The International Society for the Interaction of Mechanics and Mathematics (ISIMM) was founded in 1977. Its purpose is to promote cooperative research involving the fields of mechanics and pure mathematics.

Its Executive Committee decided that, from time to time, scholarly works relevant to the Society's interests should, by invitation, be published under its auspices. The present volume is one in this series which, it is hoped, will help to advance the objective of the Society.

The Editorial Board

Preface

Nowadays it is possible to teach and learn thermodynamics in a deductive manner: Once the general equations of irreversible thermodynamics are laid down, the specific field equations for density, motion and temperature follow by the exploitation of universal physical principles and by the restriction to a particular class of materials. The classical relations of thermostatics follow for equilibrium.

This deductive procedure is most clearly described in Chapter 1 and it is reflected over and over again in Chapters 6–13, each one of which is concerned with a different class of materials. Chapters 2–5 derive or motivate the general principles of thermodynamics and in some cases they point out their limitations.

The book has grown out of many years of teaching thermodynamics at the Johns Hopkins University in Baltimore, as well as at the Universities of Düsseldorf, Paderborn and Berlin. Students and colleagues have contributed to it by making suggestions and giving advice, and their encouragement is gratefully acknowledged here. Special thanks are due to Mr G. M. Kremer who carefully read the manuscript and corrected many errors. Frau H. Berger typed, retyped and corrected the manuscript with infinite patience.

Ingo Müller

Contents

1 Nature and Scope of Thermodynamics—Illustrated for a Viscous, Heat-conducting Fluid

This chapter defines thermodynamics of a single body as a field theory of density, motion and temperature. It shows how equations of balance and constitutive equations combine to give the field equations of thermodynamics and describes the need for restrictive conditions on the constitutive functions. Such conditions are material objectivity, the entropy principle and thermodynamic stability which are formulated here and exploited for viscous, heat-conducting fluids.

In this manner the chapter gives a first illustration of the procedure of thermodynamics and provides an appreciation of obtainable results. The chapter avoids subtleties concerning the introduction of the absolute temperature and it contains a bare minimum of proofs and motivations. It relies on some prior knowledge on the part of the reader, because the basic equations of balance, and other tenets of thermodynamics are used before these have been developed systematically in subsequent chapters.

1.1 Thermodynamic processes and the objectives of the constitutive theory

1.1.1 Thermodynamic fields in fluids

Thermodynamics of fluids is a field theory with the primary objective of determining the five fields of

density $\rho(x_n, t)$
velocity $v_i(x_n, t)$ and (1.1)
(absolute) temperature $T(x_n, t)$

of all particles of the fluid and for all times.

The density ρ of a particle is a measure of its inertia and the temperature T determines how hot the particle is.

In order to determine the thermodynamic fields (1) one needs field equations and these are based on the equations of balance of mechanics and thermodynamics.

1.1.2 Equations of balance

The equations of balance of mass, momentum and energy read, for regular points of the fluid,

$$\frac{\partial \rho}{\partial t}+\frac{\partial \rho v_j}{\partial x_j}=0,$$

$$\frac{\partial \rho v_i}{\partial t}+\frac{\partial}{\partial x_j}(\rho v_j v_i - t_{ij})=\rho f_i, \tag{1.2}$$

$$\frac{\partial \rho(\varepsilon+\frac{1}{2}v^2)}{\partial t}+\frac{\partial}{\partial x_j}(\rho(\varepsilon+\tfrac{1}{2}v^2)v_j - t_{ij}v_i + q_j)=\rho f_i v_i + \rho r,$$

where f_i is the specific body force and r is the specific absorption of radiation. f_i and r will usually be supposed to be given functions of $\mathbf{x}$ and t. The equations (2) are also known as the equation of continuity, Newton's equation of motion and the first law of thermodynamics, in this order.

The equations of balance of mass, momentum and energy on a singular surface with the unit normal n_i and the normal speed $\underset{s}{v}_\perp$ read

$$[\rho(v_i n_i - \underset{s}{v}_\perp)]=0,$$

$$[\rho v_j(v_i n_i - \underset{s}{v}_\perp) - t_{ij}n_i]=0, \tag{1.3}$$

$$[\rho(\varepsilon+\tfrac{1}{2}v^2)(v_i n_i - \underset{s}{v}_\perp) - t_{ij}n_i v_j + q_i n_i]=0,$$

provided that the surface does not have properties of its own, like surface tension, etc. The square brackets denote the difference of the bracketed quantity on the two sides of the surface.

While the equations of balance (2) are five in number, they cannot serve as field equations for ρ, v_i and T in the present form even if the body force and the radiation supply are prescribed. Indeed, T does not occur in (2) and, instead, new fields have appeared, viz. the stress t_{ij}, the heat flux q_i and the specific internal energy ε. Thus the system (2) is underdetermined, since it contains far less equations than unknown fields.

In this situation one must rely on experience, which indicates that stress, heat flux and internal energy are dependent on the fields of density, velocity and temperature in a materially dependent manner through *constitutive equations.*

1.1.3 Constitutive equations

Experience with viscous, heat conductive fluids indicates that t_{ij}, q_i and ε at a point x_n and time t depend on ρ, v_i and T at that point and time and on v_i and T

in the immediate neighbourhood. Accordingly the constitutive equations for such fluids have the general forms

$$
\begin{aligned}
t_{ij} &= \mathscr{t}_{ij}\left(\rho, v_r, T, \frac{\partial v_r}{\partial x_s}, \frac{\partial T}{\partial x_r}\right),\\
q_i &= \mathscr{Q}_i\left(\rho, v_r, T, \frac{\partial v_r}{\partial x_s}, \frac{\partial T}{\partial x_r}\right),\\
\varepsilon &= \mathfrak{e}\left(\rho, v_r, T, \frac{\partial v_r}{\partial x_s}, \frac{\partial T}{\partial x_r}\right).
\end{aligned}
\tag{1.4}
$$

The symbols $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ represent the constitutive functions.

The set of variables in (4) defines the class of viscous, heat-conducting fluids for the purpose of the theory, and the form of the functions $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ defines a particular fluid within that class.

1.1.4 Thermodynamic processes

If the functions $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ were known explicitly for a particular fluid, we would be able to eliminate t_{ij}, q_i and ε between the equations of balance (2) and the constitutive relations (4). Hence a system of five explicit field equations appears for the determination of the five thermodynamic fields ρ, v_i and T. A solution of these field equations is called a *thermodynamic process*.

Thus, if indeed the functions $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ were known for a fluid, the objective of thermodynamics, viz. the determination of ρ, v_i and T, would be reached by finding solutions of a system of partial differential equations for given initial and boundary values. This would be entirely a mathematical problem—a difficult one, to be sure, but an explicit one.

1.1.5 The objectives of the constitutive theory and its tools

In reality the situation in thermodynamics is much worse than this. Indeed, there is not a single fluid for which we do know the explicit forms of the constitutive functions $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ in the whole range of variables.

For this reason thermodynamicists are making every effort to get to know the functions $\mathscr{t}_{ij}$, $\mathscr{Q}_i$ and $\mathfrak{e}$ better. They attempt to restrict the generality of these functions and, if possible, reduce them to a small number of coefficients whose values could then be measured. Such efforts belong to the *thermodynamic constitutive theory*, which is the main concern of this book.

The main tools of the constitutive theory for restricting the constitutive functions are universal physical principles which have been abstracted from long experience with bodies of arbitrary material. The most important ones among such principles are the *principle of material frame indifference*, the *entropy principle* and *thermodynamic stability*.

Also, sometimes the constitutive functions of a body are *a priori* known to