

THE THERMODYNAMICS OF FLUID SYSTEMS

L. C. WOODS



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CLARENDON PRESS · OXFORD

Oxford University Press, Walton Street, Oxford OX2 6DP

Oxford New York Toronto
Delhi Bombay Calcutta Madras Karachi
Petaling Jaya Singapore Hong Kong Tokyo
Nairobi Dar es Salaam Cape Town
Melbourne Auckland
and associated companies in
Beirut Berlin Ibadan Nicosia

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Published in the United States
by Oxford University Press, New York

© Oxford University Press 1975

First published 1975

Paperback edition 1985

Reprinted with corrections 1986

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British Library Cataloguing in Publication Data

Woods, L. C.

The thermodynamics of fluid systems. – (Oxford
engineering science; 2)

I. Title II. Series

536'.7 QC145.4.T5

ISBN 0 19 856180 6

Library of Congress Cataloging in Publication Data

Woods, L. C. (Leslie Colin), 1922 –

The thermodynamics of fluid systems.
(Oxford engineering science series; 2)

Bibliography: p.

Includes index.

1. Thermodynamics equilibrium. 2. Irreversible
processes. 3. Fluids – Thermal properties. I. Title.
II. Series.

QC318.T47W66 1985 536'.7 85-21836

ISBN 0 19 856180 6 (pbk.)

Printed and bound in Great Britain by
Biddles Ltd, Guildford and King's Lynn

PREFACE

A SUITABLE sub-title for this book would have been 'The time-variable in thermodynamics', for throughout the emphasis is placed on the role of time scales, in determining both the state coordinates of equilibrium thermodynamics (Part I) and the affinities or thermodynamic forces of irreversible processes (Part II). The notion that the entropy of a system depends *inter alia* on the time scale on which it is observed (or equivalently on how detailed is the observer's information about it) is employed in both parts to make clear the unity of classical, kinetic, statistical, and process thermodynamics. This practical approach also enables us to resolve the occasional paradoxes that arise with entropy and its increase in isolated systems, for these can usually be traced to the false belief in the existence of an absolute entropy, a belief unfortunately encouraged by the currently-popular axiomatic treatments of thermodynamics. Thermodynamics is, above all, an approximating science in which it is necessary not only to understand the various limit forms it can take but also the physics of the asymptotics involved.

My aim initially was to write a concise account of the thermodynamics of irreversible processes in gases, plasmas, and other fluids, placing a greater emphasis on the underlying assumptions and less on chemical applications than the few reliable texts presently available. But it became clear at an early stage of writing that the key and unavoidable hypothesis of 'local thermodynamic equilibrium' needs much more elaboration than it usually receives. The concept of thermodynamic equilibrium is not nearly as simple and precise as most accounts imply; and without a clear idea of its meaning, it is pointless for the student to advance to process thermodynamics. Thus Part I (on equilibrium thermodynamics) was written to serve both as a survey of the principal ideas of the subject and, because of its emphasis on the relative nature of 'equilibrium', as a suitable introduction to Part II.

Part I starts with what may be called 'engineering' thermodynamics, for it deals with long-time-scale external processes; it is based on the first three laws of thermodynamics, which combine to define an entropy S via the fundamental formula $T dS = dU + p dV$. The observer's time scale is then progressively shortened, and at each step terms added to the fundamental equation to represent the increasing knowledge assumed of the system; and so we proceed through 'chemical' thermodynamics and 'kinetic' thermodynamics to the ultimate description contained in statistical thermodynamics. By introducing an internal coordinate ξ , defined over an 'interior' space y , we are able to transform the fundamental expression for $T dS$ into the prescription $S = -k \sum \xi_i \ln \xi_i$, which, unconstrained, holds on all time scales. It is the constraints that are added to turn the prescription into a genuine

definition that are time-scale dependent, and the shorter the observer's time scale the greater the number of constraints that must be imposed.

I hope this novel approach will provide a useful skeletal survey of basic thermodynamics suitable for final-year students in the physical sciences.

In Part II the concepts of process thermodynamics (often confusingly termed 'non-equilibrium' thermodynamics, despite the fact that local thermodynamic *equilibrium* is a *sine qua non* ingredient) are explained and applied to a variety of fluid phenomena. There are four basic ideas.

First there is the separation of processes into reversible and irreversible elements, a division that depends on the physical model assumed to represent the system. And when the reversible changes of entropy are known, the rate σ at which entropy is irreversibly created can be expressed as a bilinear form, say, $\sigma = \mathbf{JX}$, where \mathbf{J} and \mathbf{X} are vectors representing the various processes and thermodynamic forces in the system. In all this time scales play an important part. As σ is non-negative, we have the basic inequality $\sigma = \mathbf{JX} \geq 0$, which has much the same role in process thermodynamics as does the fundamental equation $dS = T^{-1}dU + T^{-1}p dV + \dots = Z dY$, say, for equilibrium thermodynamics. From the latter we use the fact that dS is the exact differential of a function $S = S(Y)$ to infer the existence of state equations $Z = Z(Y)$; and likewise as $\sigma \geq 0$ requires \mathbf{J} and \mathbf{X} to vanish together, we may infer constitutive relations $\mathbf{J} = \mathbf{J}(\mathbf{X})$ from the bilinear form.

With the assumption of linear constitutive relations, say $\mathbf{J} = \mathbf{LX}$, where \mathbf{L} is a phenomenological matrix, we come to the second basic idea of process thermodynamics, namely, the existence of reciprocal relations between the coefficients L_{ij} of \mathbf{L} , which in the simplest case are $L_{ij} = L_{ji}$. In essence, these relations are due to W. Thomson (Lord Kelvin), although it is usual to dismiss his arguments as being too intuitive to offer a convincing proof. On the other hand, the accepted treatment, due to L. Onsager, relies too much on the analogy taken to exist between the regression of large thermodynamic fluctuations and macroscopic processes like heat or current flux that persist not only in stationary flow conditions but, more importantly, in systems pressed to the (thermodynamic) limit at which fluctuations strictly vanish. The new approach offered in this book (along with accounts of the works of Thomson and Onsager) resembles Thomson's in being genuinely 'macroscopic'. By the time-scale arguments required to draw the distinction between reversibility and irreversibility, it is shown that the essential nature of the reciprocal relations is that they ensure that the entropy production rate $\sigma = \mathbf{XLX}$ is due only to irreversible processes.

The two remaining basic concepts are common to all branches of macroscopic physics. They are 'reference-frame indifference', which requires the constitutive relations to be expressible in covariant form, and 'material invariance', by which spatial symmetries known to exist in the system enable us to reduce substantially the number of independent elements appearing in

L. Particular attention has been given to the lateral isotropy of magneto-plasmas, in which the magnetic field imposes a characteristic direction on the medium.

The use of internal coordinates ξ permits a great extension in the scope of process thermodynamics. And when constitutive relations for $\xi(t)$ are known or assumed, some or all of these coordinates may be eliminated with the effect of replacing the instantaneous constitutive relation $\mathbf{J} = \mathbf{L}\mathbf{X}$ by the integral relation $\mathbf{J}(t) = \int_{-\infty}^t \psi(t-t')\mathbf{X}(t') dt'$, where $\psi(t)$ is a phenomenological response function. If, further, owing to thermodynamic fluctuations, the $\xi(t)$ are assumed to be stochastic processes, the theory leads on to the important fluctuation-dissipation theorem, of which the earliest examples are contained in Einstein's work on Brownian motion and Nyquist's on Johnson noise.

Fluid mixtures are systems for which the systematic approach of process thermodynamics is particularly useful, for the number of possible processes and cross-couplings between them may be quite large. A general account of mixture theory, which includes the effects of mass transfer between the components, is followed by applications to two important examples, namely, magneto-plasmas and helium II. A magneto-plasma can be described adequately by a two-fluid theory on a certain time scale and is a good example of an anisotropic medium. Helium II, on the other hand, has the interesting feature (rather neglected in standard treatments) that its normal and super-fluid components can exchange mass elements. These aspects have been pursued to the stage of obtaining some new results for each mixture. Rotating helium II, which is an anisotropic medium, is also given some attention.

Kinetic constitutive relations are described in the final chapter. The set S_1, S_2, \dots, S_r of entropies for the one-particle (F_1), two-particle (F_2), ... r -particle (F_r) distribution functions yields a sequence of non-negative entropy production rates $\dot{S}_1, \dot{S}_2, \dots, \dot{S}_r$, from which may be inferred constitutive relations for F_1, F_2, \dots of increasing accuracy. This approach yields the kinetic equations of Boltzmann, Bogoliubov, and others, and may have some merit over the usual methods of closing the BBGKY hierarchy of equations. In any case it reveals the close similarity between kinetic equations and the constitutive relations of macroscopic fluid dynamics.

Part II will, I hope, be of interest to graduates working in continuum mechanics and other branches of macroscopic physics.

Among the many relevant texts and articles I have studied—of which only those essential to the textual argument have been cited—I am particularly indebted to the work of S. R. de Groot and P. Mazur (1962), which first engaged my attention in the thermodynamics of irreversible processes. And perhaps it is right to admit too that a growing aversion to axiomatic thermodynamics, with its *penchant* for substituting deductive mathematical constructions in place of physics, has stimulated me to write this book, and in it to

emphasize the approximations inherent in thermodynamics, or at least those approximations associated with time scales. It is, of course, the existence of such approximations that makes thermodynamics such a rich and diverse branch of physics.

I am grateful to both H. Troughton and Stanley Morris for help with checking the manuscript and proofs, to Mrs. Ina Godwin for her excellent typing of rather complicated material, and finally to the Delegates of the Oxford University Press for accepting my biased recommendation as a series editor that the work was suitable for publication in the Oxford Engineering Science Series.

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August, 1974*

L.C.W.

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PART I
EQUILIBRIUM THERMODYNAMICS

THERMODYNAMIC VARIABLES AND PROCESSES

1. Thermodynamic systems

1.1. Macroscopic variables

BEFORE describing a thermodynamic system, we shall consider some of the general properties of a real physical system consisting of matter and radiation lying in a finite region of space. Because of the atomic constitution of matter, there are small lengths and times, termed 'microscopic', in which substantial changes in the properties of individual particles (molecules, atoms, protons, electrons, photons, etc.) can occur. Thus, for example, under STP conditions in air the momentum mw of a typical molecule of mass m and velocity w is significantly changed over a distance of a mean free path λ ($\approx 10^{-5}$ cm) and in a mean free time $\tau = \lambda/|w|$ ($\approx 10^{-10}$ s). On the other hand, the averages of particle properties like the momentum per unit mass $v = \langle mw \rangle / \langle m \rangle$ and the energy per unit mass $u = \langle \frac{1}{2}mw^2 \rangle / \langle m \rangle$ taken over the enormous number of particles ($\approx 10^7$) in a microscopic volume element ($\approx 10^{-12}$ cm³) usually change over much larger length L and time \mathcal{T} scales. Such averages are termed 'macroscopic' properties and L and \mathcal{T} are the macroscopic length and time scales. Provided $L \gg \lambda$ and $\mathcal{T} \gg \tau$, we can introduce macroscopic infinitesimals $|dr|$ and dt of length and time that are large on a microscopic scale but small on a macroscopic scale. Then, save in exceptional regions, macroscopic properties like v and u will be smooth functions of the position vector r and of the time variable t , changing by small increments $|dv|$ and du over $|dr|$ and dt .

The study of the spatial and time fields of macroscopic variables like $u(r, t)$ is termed 'continuum mechanics' if $|dr| \gg \lambda$, $dt \gg \tau$, for in this case the particulate nature of matter is completely submerged and, further, the scale lengths are such that particle behaviour is aptly described as being 'collision-dominated'. This has the consequence that many physical effects—like, for example, the mechanical stress—are transmitted *locally*, and so can be described by differential equations. As the average distance between particles ($\approx 10^{-7}$ cm for air at STP) is considerably less than λ , smooth functions $u(r, t)$ can be defined for $|dr|$ and dt much less than λ and τ . Under these circumstances the particles are 'collision-free', physical effects are transmitted on a global scale, and a more detailed description of the behaviour of the macroscopic fields is necessary. This is the province of 'kinetic theory', which

will be discussed in a later chapter. In both kinetic theory and continuum mechanics the dependent variables are macroscopic and the independent variables include r and t . Equilibrium thermodynamics is also concerned with macroscopic variables, its principal results being relationships between certain of the variables occurring in the field theories; such relationships are independent of r and t , which may, however, play parametric roles.

1.2. *Equilibrium on the observer's length and time scales*

An omnipresent observer could specify the macroscopic state of a physical system P , say, at a given time t , by giving all the macroscopic properties of P , both physical and chemical, as functions of r . A human observer must be content with a greatly reduced set of macroscopic variables, and the problem of defining a thermodynamic system lies in how to specify this set, say $\{x_1, x_2, \dots\}$, for a given system P and a given observer Q . The observer's time and length scales, say \mathcal{T} and \mathcal{L} , are the most important elements in the problem. These scales, which depend on the observer's objectives and knowledge, must be compared with the variety of time and length scales occurring naturally in P , due either to purely internal changes or to interactions between P and its environment. For example, if the variable x_r has a maximum gradient x'_r , the length $L = x_r/x'_r$ occurs naturally in P and it is reasonable to assume that over a length \mathcal{L} , where $\mathcal{L} \ll L$, it is permissible for Q to ignore gradients in x_r , that is, to take x_r as uniform in P . The variables in equilibrium thermodynamics are always assumed to be uniform; departures from uniformity lie within the ambit of 'process thermodynamics' to be described in Part II.

Similarly, a further reduction in the set $\{x_r\}$ defining the state of P results if 'temporal equilibrium' may be assumed by Q for some of the variables. The role of the time variable in thermodynamics is particularly important, although not easily explained at the beginning of the subject; the following description is amplified in a later section (§ 19.1). There are two quite distinct kinds of temporal equilibrium in thermodynamics. To explain these we shall introduce the natural time scales

$$\tau_r = (x_r^{\text{eq}} - x_r)/\dot{x}_r, \quad (r = 1, 2, \dots), \quad (1.1)$$

where x_r^{eq} denotes the value x_r would attain as $t/\tau_r \rightarrow \infty$. Now order the time scales so that $\tau_1 \geq \tau_2 \geq \tau_3 \dots$ and suppose that Q 's time scale \mathcal{T} satisfies

$$\tau_m \gg \mathcal{T} \gg \tau_{m+n}, \quad (1.2)$$

where τ_m is the least scale and τ_{m+n} is the greatest scale that will satisfy the gross inequalities in (1.2).† On Q 's time scale the variables x_r , $r = 1, 2, \dots, m-1$, are said to be in 'frozen' equilibrium, and Q observes them to be

† It is impossible to give such inequalities precision out of physical context; the reader should think in terms of factors of 10^2 or more.

constants in P . On the other hand, Q observes that the variables x_r , $r > m+n$, can change so rapidly that they never deviate measurably from their equilibrium values x_r^{eq} ; such variables are in 'relaxed' equilibrium. Stability requires that x_r^{eq} depend only on the variables x_s , $s < r$, that change more slowly than x_r . Thus for the system (P, Q) (P observed by Q), the relevant thermodynamic variables are the set $\{x_r\}$, $m \leq r \leq m+n$, which change more or less on Q 's time scale.

1.3. Thermodynamic systems

The time scale \mathcal{T} is not the only observer-dependent element in thermodynamics: two observers may have the same \mathcal{T} but different views on what is important in P . For example, Q_1 may hypothesise that the ionization level χ is an important variable in a strong shock wave and thus include χ as a thermodynamic variable, whereas Q_2 may consider χ unimportant. And with different objectives they could both be correct. Such subjective aspects are, of course, present in all idealized models of real physical systems and can never be completely removed.

The system (P, Q) is called a *thermodynamic system* and $\{x_r\}$, $m \leq r \leq m+n$, are its *thermodynamic variables*. The principal objective of classical thermodynamics is to establish relationships involving just these variables and their derivatives. A subset of these variables, termed *thermodynamic coordinates*, serves to define a state-space, and the remaining variables are then functions of state. The coordinates may be chosen in a variety of ways, and it is clearly convenient to include among them any of the x_r known to be constant (on Q 's time scale). Those (thermodynamic) variables that are already familiar from mechanics and electromagnetism like pressure p , volume V , mass M , magnetic flux \mathbf{B} , and electric field \mathbf{E} are accepted as primitive concepts, and the derivation of additional variables, entirely thermodynamic in origin, is the first task in the development of thermodynamics.

To derive new thermal variables it is necessary to assign some physical properties to the thermodynamic system, distinct from those just mentioned. There are several ways of going about this, all equally valid but with distinct metaphysics. The usual textbook treatment is to introduce the additional physical properties implicitly via the so-called 'laws' of thermodynamics, and with the aid of 'walls' that separate the system from its immediate surroundings and that limit in various ways the nature of the exchanges between them. In this axiomatic approach, of which there are several variants, the thermal variables are defined in terms of the non-thermal ones, so that their intrinsic physical significance is not clarified. This is possible because on a long time scale the state may be defined by coordinates chosen from the list of variables accepted as primitive or non-thermal. For example, the simplest thermodynamic system is a gas of a single chemical constituent in a container, and on a long time scale its state coordinates may be taken to be its pressure p

and volume V (in what follows such a system will be termed a 'simple' gas system). Alternatively we can accept the atomic nature of matter and directly attribute macroscopic thermal variables to the system, such as the internal energy u defined above, with a consequent reduction in the 'laws' required. In the prevailing philosophy of continuum mechanics it is usual to eschew deductions from a knowledge of the existence of atoms, and this fashion will be followed for the present.

2. The empirical temperature

2.1. Adiabatic walls

'Temperature' is the most important of the entirely thermodynamic properties. To define it we first need to introduce the concept of a 'wall' C that separates a system P from its surroundings P^* . At one extreme C need have no physical properties at all, save that of merely defining the extent of P ; at the opposite end of the scale C may isolate P completely from P^* , by which is meant that there are no changes possible in P^* able to affect the state of P , and vice versa. Such isolation is an idealized concept for it is a well-established principle that no part of the universe can be completely isolated from the rest of the (visible) universe. However if the observer's time scale \mathcal{T} is very small compared with the transit times of various phenomena through C , we may assert that P is effectively isolated from the effects of such phenomena. Clearly \mathcal{T} must be sufficiently small for C to appear to Q as being impermeable, rigid, and of infinite electrical conductivity (to exclude electromagnetic fields). These properties will exclude mass and work transfers across (C, Q) (wall C observed on Q 's time scale), but experimentally it is found that they are insufficient to isolate P completely. In addition, C must possess a special thermal property that cannot be defined in terms of primitive concepts. This property is called *adiabaticity* and is found to be imperfectly present in varying degrees as the chemical composition and physical structure of C is changed.

Suppose (C, Q) isolates P from mass and work transfers, and let τ_q be the least time for a measurable change to occur in the state of P after all possible changes in P^* .† Then (C, Q) is characterized as follows:‡

if $\mathcal{T} \ll \tau_q$, (C, Q) is *adiabatic*;

if $\mathcal{T} \gg \tau_q$, (C, Q) is *diathermic*.

† Of course the important change we have in mind here is the placing of a heat source in contact with C , but the concept of heat follows later from the first law of thermodynamics, hence our circumlocution.

‡ Similar inequalities may be adopted to define 'open' and 'closed' systems

$$\mathcal{T} \ll \tau_D, (C, Q) \text{ is closed}; \quad \mathcal{T} \gg \tau_D, (C, Q) \text{ is open},$$

where τ_D is a mass diffusion time. Consideration of open systems will be deferred to § 14.

An impermeable wall that possesses adiabaticity, but which may be flexible, may admit electromagnetic fields and currents to P , and could allow mechanical devices to stir the medium of P , will be called an *adiabatic* wall. Armed with the concept of adiabatic walls, we can now introduce temperature; in the sequel the role of the observer will be supposed understood and omitted from the account.

2.2. Thermal equilibrium

Consider two adjacent systems, P_1 in state X_1 defined by m_1 coordinates and P_2 in a state X_2 defined by m_2 coordinates, isolated from their surroundings but not necessarily from each other. If P_1 and P_2 are isolated from each other, the state of the composite system (X_1, X_2) will require $(m_1 + m_2)$ coordinates to define it, whereas, if P_1 and P_2 are in some form of contact, fewer than $(m_1 + m_2)$ coordinates will be required to define (X_1, X_2) . This contact will permit an exchange between P_1 and P_2 . For example, if P_1 and P_2 are two simple gas systems, $X_1 = (p_1, V_1)$, $X_2 = (p_2, V_2)$, and if they are separated by a perfectly flexible membrane, p_1 will equal p_2 and the composite system is completely defined by (p_1, V_1, V_2) . Should p_1 not equal p_2 the membrane will move to make the pressures equal and P_1 will do work on P_2 or vice versa.

Again, if P_1 and P_2 are first isolated from one another by a rigid adiabatic wall, then $(X_1, X_2) = (p_1, V_1, p_2, V_2)$; if this partition is now replaced by a diathermic wall it is found that P_1 and P_2 move to new equilibrium states in which any three of p_1, V_1, p_2, V_2 are sufficient to define the composite state. Hence there must exist a definite relationship

$$F(p_1, V_1, p_2, V_2) = 0, \quad (2.1)$$

and P_1 and P_2 are said to be in *thermal equilibrium* with each other. Similarly, in the general composite state space of $(m_1 + m_2)$ coordinates, the thermal equilibrium states will lie on a $(m_1 + m_2 - 1)$ surface.

2.3. Zeroth law and empirical temperature

The first of the four fundamental laws of thermodynamics, called the 'zeroth law' (being discovered last), states

0. Two systems in thermal equilibrium with a third are in thermal equilibrium with each other.

Actual thermal contact via a diathermic partition is not necessary here; we mean rather that if such contact were established, there would be no change of state for the two systems involved. It is sufficient to consider three simple systems P_1, P_2 , and P_3 . Let P_3 be in thermal equilibrium with each of P_1 and P_2 , then functional relations

$$F_{13}(p_1, V_1, p_3, V_3) = 0 \quad \text{and} \quad F_{23}(p_2, V_2, p_3, V_3) = 0 \quad (2.2)$$