Generalized Thermodynamics

Fundamental Theories of Physics

An International Book Series on The Fundamental Theories of Physics: Their Clarification, Development and Application

Volume 124

Generalized Thermodynamics

The Thermodynamics of Irreversible Processes and Generalized Hydrodynamics

by

Byung Chan Eu
McGill University, Montreal, Canada

KLUWER ACADEMIC PUBLISHERS
NEW YORK, BOSTON, DORDRECHT, LONDON, MOSCOW

eBook ISBN: 0-306-48049-2
Print ISBN: 1-4020-0788-4

Created in the United States of America

Visit Kluwer Online at: http://kluweronline.com
and Kluwer's eBookstore at: http://ebooks.kluweronline.com

This work is · · ·

to the memory of the days of youth

of lavender dreams,

the dreams of light, ...,

in the sun-woven shade of the lilac

on the old campus in Seoul.

Contents

Preface

Despite a long history of almost 180 years stretching back to the times of Carnot and, later, Clausius and Lord Kelvin, amongst others following him, the subject of thermodynamics has not as yet seen its full maturity, in the sense that the theory of irreversible processes has remained incomplete. The works of L. Onsager, J. Meixner, I. Prigogine on the thermodynamics of linear irreversible processes are, in effect, the early efforts toward the desired goal of giving an adequate description of irreversible processes, but their theory is confined to near-equilibrium phenomena. The works in recent years by various research workers on the extension of the aforementioned thermodynamic theory of linear irreversible processes are further efforts toward the goal mentioned. The present work is another of such efforts and a contribution to the subject of generalizing the thermodynamics of reversible processes, namely, equilibrium thermodynamics, to that of irreversible processes—non-equilibrium thermodynamics, without being restricted to linear irreversible processes. In this context the terms 'far removed from equilibrium' is often used in the literature, and such states of macroscopic systems and non-linear irreversible phenomena in them are the objects of interest in this work.

The thermodynamics of processes, either reversible or irreversible, is a continuum mechanical theory of matter and energy and their exchange between different parts of the system, and as such it makes no direct reference to the molecules constituting the substance under consideration. In thermodynamics the nature of molecules composing the continuum matter manifests itself quite indirectly in the constitutive equations for the substance, such as the equation of state, the caloric equation of state, the material functions such as viscosity, thermal conductivity, and diffusion coefficients, and other thermophysical properties. The constitutive equation for a given macroscopic property of a substance contains parameters reflecting the nature of molecules in the substance, but unlike statistical mechanics thermodynamics does not start with individual molecules in its treatment of macroscopic properties. The forms and the values of the parameters in the constitutive equations of different substances for a given property, however, can be classified into different categories according to homologous series of substances, and thermodynamics distinguishes molecular systems in such a sense, but the basic mathematical structure of thermodynamics, either reversible or irreversible, remains generic to continuum matter. In this universality of its mathematical structure conforming to the laws of thermodynamics lies the power, usefulness, and formal beauty of thermodynamics for treating macroscopic phenomena and relating them to each other. Our principal objective is then to acquire a thermodynamic theory of irreversible processes in a form as universal as possible so that it applies to diverse macroscopic phenomena in equally diverse systems in strict conformity with the laws of thermodynamics. Since often in the literature and everyday life the term thermodynamics refers to the thermodynamics of reversible processes, namely, thermostatics, to avoid confusion we adopt the term 'generalized thermodynamics' for the thermodynamic theory of irreversible processes, although in this work we often use simply the term 'thermodynamics' in a general sense covering both reversible and irreversible, or equilibrium and non-equilibrium, processes. The term 'generalized thermodynamics' was coined by L. Tisza to mean thermodynamics of irreversible processes in my personal interpretation of the term. And I believe it is an appropriate terminology to use for the subject covered in this work, which is the continuum mechanics part of the author's study of non-equilibrium statistical mechanics and irreversible thermodynamics. For this reason I have consciously tried to avoid any reliance on statistical mechanics or the kinetic theory of matter in this monograph.

My interest in thermodynamics and, in particular, in the thermodynamics of irreversible processes goes back to the late fifties of the last century, when Professor Shoon Kyung Kim of Temple University, then at Seoul National University, gave a few lectures on Prigogine's work on irreversible processes toward the end of his course on thermodynamics. The subject left a deep and indelible impression on me. Since then, despite my unanticipated but fortunate excursion into the phenomena and theories of molecular scattering in the early part of my research life until I was able to return fully to my initial youthful interest in the mid 1970s, the desire to learn about the subject matter more fully has never left me, but I could only make some intermittent stabs at the subject during the intervening years. The present work is a synthesis of what I have learned and studied on the subject of the thermodynamics of irreversible processes since 1975. I hope that what I have presented in this monograph is perceived as sufficiently coherent in the eyes of the reader and, consequently, reading it gives some benefits to the reader who may have just begun to learn about the subject or may have already acquired a considerable body of knowledge of the subject either along the line presented in this work or in the approaches made by other research workers in the field.

As is well recognized, the subject of thermodynamics is basically founded on the pair of empirical laws known as the first and second laws of thermodynamics, and enunciated by the founders of thermodynamics. In particular, the second law of thermodynamics, being a literal statement based on Sadi Carnot's deep insights into empirical observations of natural phenomena associated with heat and its transformation into energy, requires a precise mathematical representation so that a mathematical theory of thermodynamic processes in macroscopic systems can be unambiguously formulated in conformity with the laws of thermodynamics. As has been well known, Clausius obtained such a representation only for the reversible process part of the second law of thermodynamics, leaving the representation of the irreversible process part unaccomplished. We have managed to acquire the desired mathematical representation for the second law of thermodynamics for both reversible and irreversible processes. Such a full mathematical representation gives rise to the notion of calortropy, which extends to irreversible processes the notion of entropy that was discovered by Clausius for reversible processes only and is in the foundations of equilibrium thermodynamics known to us to this day. The notion of calortropy now is in the foundations of the thermodynamics of irreversible processes and the attendant generalized hydrodynamics for flow processes in macroscopic systems that have been presented in this monograph. Of course, the Clausius entropy is recovered from the calortropy in the limit of reversible processes. Interestingly, generalized hydrodynamics is an integral part of thermodynamics of irreversible processes; it reduces to the classical hydrodynamics of Navier, Stokes, and Fourier, as the constitutive equations for stress and heat flow become linear with respect to the thermodynamic forces and the system approaches states near equilibrium. It is significant that hydrodynamics can be framed within the bounds of the laws of thermodynamics even if the hydrodynamic processes are highly non-linear and far removed from equilibrium. Applications of such generalized hydrodynamics are discussed in this monograph.

The generalization of thermodynamics presented in this monograph requires an extension of the thermodynamic space of classical thermodynamics so as to include the non-conserved variables necessary for the description of transport processes in the system. Similar extensions are also made in other approaches recently proposed by various authors under the generic name of 'extended irreversible thermodynamics', but in these approaches the non-equilibrium entropy is simply a postulate based on a plausibility argument, but not a quantity deduced from the second law of thermodynamics as originally stated by Clausius and Lord Kelvin. In this respect the present theory and the other theories mentioned earlier differ, and I believe this difference is significant. Nevertheless, there are many features which are similar except for the important constitutive equations for non-conserved variables that turn out to be crucial in validating the theory in comparison with experiment and accounting for the mode of energy and matter dissipation from a useful to a less useful form in a given process. I believe that the success or failure of a theory of irreversible processes can be decided by the capability of the attendant hydrodynamic equations, whose applications to practical problems require laborious and time consuming work.
I would like to acknowledge the collaborations with my former graduate students, post-doctoral fellows, and visiting associates who have played indispensable roles in developing, refining, and testing the theories making up the body of this work. I am grateful to all of them for their friendly collaborative companionship and valuable contributions along the journey which otherwise would have been lonely and, perhaps, even not possible by myself alone.

In preparing the camera-ready manuscript of this monograph Dr. Kyunil Rah and my son David have rendered valuable assistance by drawing some of the figures. I would like to thank them for their assistance. I would also like to thank the Natural Sciences and Engineering Research Council of Canada for their continuous financial support throughout the project of non-equilibrium statistical mechanics which I have carried out in the past. Finally, but more than anything else, I would like to express my deepest gratitude to my wife Hui Young for her undiminished patience, which has more than lightened the weight of labor required by research and for her continuous encouragements and devotion throughout all the years spent on my efforts toward this project in the past.

Montreal
December, 2001

B. C. E.