Extended Irreversible Thermodynamics

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Fourth Edition

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Preface to the Fourth Edition

The fast progress in many areas of research related to non-equilibrium thermodynamics has prompted us to write a fourth edition of this book. Like in the previous editions, our main concern is to open the subject to the widest audience, including students, teachers, and researchers in physics, chemistry, engineering, biology, and materials sciences. Our objective is to present a general view on several open problems arising in non-equilibrium situations, and to afford a wide perspective of applications illustrating their practical outcomes and consequences. A better comprehension of the foundations is generally correlated to an increase of the range of applications, implying mutual feedback and cross fertilization. Truly, thermodynamic methods are widely used in many areas of science but, surprisingly, the active dynamism of thermodynamics as a field on its own is not sufficiently perceived outside a relatively reduced number of specialized researchers.

Extended irreversible thermodynamics (EIT) goes beyond the classical formalisms based on the local equilibrium hypothesis; it was also referred to in an earlier publication by the authors (Lebon et al. 1992) as a *thermodynamics of the third type*, as it provides a bridge between classical irreversible thermodynamics and rational thermodynamics, enlarging at the same time their respective range of application. The salient feature of the theory is that the fluxes are incorporated into the set of basic variables. The urge and interest of elevating the fluxes to a central role is illustrated by our everyday experience, the fluxes of people, of goods, of money, of energy, of pollutants, of information, are among the main protagonists of our epoch of globalization. Lowering or exceeding some critical values of the fluxes may be determinant in the survival or collapse of our economical and (or) social system as it has been dramatically illustrated by financial and economical crises. Fluxes are not only essential in social sciences, but also in biology: complex and delicate networks of fluxes of matter, energy and information are basic to life. Thus, paying a special attention to the fluxes seems in tune with science and society of our time. This does not mean that they are the only possible choice for describing systems beyond local-equilibrium, but certainly they are a logical and appealing possibility, worth of exploration.

Our aim in this new edition is to update the previous versions by including new materials and new applications to parallel the vertiginous developments of modern technology. To enhance the pedagogical value of the book, we have increased the number of applications, and figures comparing theory and experimental results.

In comparison with the third edition, the present one has been extensively remodelled. Several fundamental chapters have been restructured and rooted on intuitive physics rather than on lengthy mathematical expressions. Fundamental questions as the definition of temperature, entropy, fluctuations of the fluxes, and the nature of boundary conditions are now becoming clearer than some years ago, and have deserved a new presentation. More explicitly, a new chapter 10 on heat transport at micro- and nano-scales is included; Chaps. 2, 11, 13 and 15 have been revisited in depth, and several new sections have been added throughout the book. Some particular subjects or mathematical developments which can be omitted in a first reading have been collected in boxes. Other aspects treated with detail in the authors' other books *Understanding non-equilibrium thermodynamics* (Springer 2008) and *Thermodynamics of fluids under flow* (Springer 2000) have been suppressed in this new edition. Some misprints in the previous edition have been corrected, and the set of proposed problems has been slightly enlarged and updated.

The present edition has benefited from the precious technical help of Drs. V. Méndez and V. Ortega-Cejas. We are indebted to Dr. P. Galenko for his contribution to Sect. 13.7 and for promoting the Russian translation of our book (*Rasshirenaia Neobratimaia Thermodinamika*, published by Reguliarnaia Kaoticheskaia Dinamika, Moscow-Itzvhesk, 2007). Fruitful discussions with many other colleagues, among which the late Prof. A.M. Anile, are gratefully acknowledged in the prefaces of the previous editions. David Jou and José Casas-Vázquez have benefitted from the Grants BFM2000–0351-C03–01, BFM2003–06033, FIS2006–12296-C02–01 of the Spanish Ministry of Education and Science, and 1999SGR00095, 2001SGR00186 and 2005SGR00087 of the DGR of the Generalitat of Catalonia, Georgy Lebon acknowledges partial financial support from the ESA Prodex Belgium Program.

Bellaterra, Barcelona — David Jou
Liège — José Casas-Vázquez
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Preface to the Third Edition

In writing this third edition, we proceeded having in mind two main objectives: pedagogy and physics. One of our essential concerns is indeed to open the subject to a large audience of scientists with a diversity of interests. This is the reason we have emphasized the pedagogical aspects, starting with the simplest situations before treating more complex problems. Our aim is to show that thermodynamics is not restricted to the study of purely thermal phenomena but that it largely covers many different areas, going from continuum mechanics to statistical physics, from nuclear collisions to cosmology, by passing, for instance, through chemistry, rheology and biology.

Our second objective is to stress the physical aspects in their broadest sense, i.e. trying to clarify the foundations and relating the theoretical results with experimental data and applications, rather than introducing formal and lengthy developments. Important sections of the book are devoted to the discussion of fundamental notions, such as the selection of basic variables, the definition of entropy, temperature, pressure, and chemical potential outside equilibrium and the statement of the second law. We feel that these crucial questions deserve special attention when they cross the borders of classical theories. We have included new original results and opened the door to new extensions and applications.

For the student or the researcher it may be stimulating to go beyond the classical theories and to discover a domain of new ideas, new applications, and new problems. This is what extended irreversible thermodynamics (EIT) offers nowadays: it does not pretend to solve all the problems raised in continuum physics and statistical mechanics, but it can be viewed as an emergent new global framework of non-equilibrium thermodynamics and a rapidly advancing frontier with new applications being treated and fundamental questions being asked and tentatively clarified.

This edition has been extensively remodelled compared to the first two. We have gone from 12 to 18 chapters as a result of splitting some of the former chapters into shorter ones and focusing better on the foundations and on the introduction to the basic ideas of the latest developments. As for the two preceding editions, we have clearly separated the structure of the book into three parts, namely the general theory (Part I), microscopic foundations (Part II), and selected applications (Part III). Amongst the most visible changes, we have split the general presentation of EIT into two chapters: Chap. 2 devoted to establishing the transport equations and dynamical aspects, and Chap. 3 in which we introduce the non-equilibrium equations of state emphasizing the meaning of entropy and temperature in non-equilibrium states. Comparison with the rational version of extended thermodynamics has been made more explicit. Chapter 4 shows an overview of Hamiltonian formulations, which have developed in recent years into a promising domain.

The microscopic foundations are discussed in Chaps. 5–9, with two new chapters concerning information theory and computer simulations. Both topics were already present in the former editions as subsections of other chapters, but recent developments have justified a renewed and updated presentation.

Applications cover half of the book: nine chapters from the total 18. They show that the exploration of new theoretical grounds is both an intellectual challenge and a source of new practical possibilities. Since contemporary technology strives towards higher speed, power, and miniaturization, the transport equations must incorporate memory, non-local, and non-linear effects. Compared to the generalised transport equations incorporating the aforementioned effects, EIT plays a role similar to that played by classical irreversible thermodynamics with respect to the classical transport equations. Diffusion and electrical phenomena, treated in a single chapter in the previous editions, are the subject of two different, updated chapters; the relativistic formulation has also been split into two different chapters, one devoted to the foundations and the other to cosmological applications. Finally, let us mention that a wide overview of the literature on EIT as well as the solutions to the proposed problems can be found on the http://telemaco.uab.es website.

This book, in its successive editions, has widely benefited from the fruitful suggestions and comments by colleagues, including M. Anile, J. Camacho, M. Criado-Sancho, L.S. García-Colín, M. Grmela, P.T. Landsberg, R. Luzzi, W. Muschik, D. Pavón, M. Torrisi, A. Valenti and many others. We acknowledge the financial support of the DGICyT of the Spanish Ministry of Education and Culture under Grant Nos. PB90–0676 and PB94–0718, of the DGR of the Generalitat of Catalonia, under Grant Nos. 1997SGR 00378 and 2000SGR 00095, of the Belgian Ministry of Scientific Policy under PAI Grant Nos. 21, 29 and IV 6, and a grant from the European Union in the framework of the Program of Human Capital and Mobility (European Thermodynamic Network ERB-CHR XCT 920 007).

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Preface to the First Edition

Classical irreversible thermodynamics, as developed by Onsager, Prigogine and many other authors, is based on the local-equilibrium hypothesis. Out of equilibrium, any system is assumed to depend locally on the same set of variables as when it is in equilibrium. This leads to a formal thermodynamic structure identical to that of equilibrium: intensive parameters such as temperature, pressure and chemical potentials are well-defined quantities keeping their usual meaning, thermodynamic potentials are derived as Legendre transformations and all equilibrium thermodynamic relations retain their validity. The theory based on this hypothesis has turned out to be very useful and has collected a number of successes in many practical situations.

However, the recent decade has witnessed a surge of interest in going beyond the classical formulation. There are several reasons for this. One of them is the development of experimental methods able to deal with the response of systems to high-frequency and short-wavelength perturbations, such as ultrasound propagation and light and neutron scattering. The observed results have led to generalisations of the classical hydrodynamical theories, by including memory functions or generalised transport coefficients depending on the frequency and the wavevector. This field has generated impressive progress in non-equilibrium statistical mechanics, but for the moment it has not brought about a parallel development in non-equilibrium thermodynamics. An extension of thermodynamics compatible with generalised hydrodynamics therefore appears to be a natural subject of research.

An additional reason has fostered an interest in generalising the classical transport equations, like Fourier's law for heat conduction, Fick's law for diffusion, and Newton's law for viscous flow. It is well known that after introducing these relations in the balance equations, one is led to parabolic partial-differential equations which imply that perturbations propagate with infinite speed. This behaviour is incompatible with experimental evidence and it is also disturbing from a theoretical point of view, because collective molecular effects should be expected to propagate at finite velocity, not only in a relativistic framework, but even from a non-relativistic point of view. This unpleasant property can be avoided by taking into account the finite nonvanishing relaxation time of the respective fluxes, e.g. heat flux, diffusion flux, momentum flux, sometimes generically called dissipative fluxes. The subsequent equations are however not compatible with the classical non-equilibrium thermodynamics, since they lead in some circumstances to negative entropy production. Thus, a thermodynamic theory compatible with these phenomena is highly desirable, because it may provide new insights into the meaning and definition of fundamental thermodynamic quantities, as entropy and temperature, and may clarify the limits of validity of the local-equilibrium hypothesis and of the usual formulations of the second law out of equilibrium.

The former problems are not merely academic. It has been observed in several systems that the dissipative fluxes are characterized by long relaxation times. Typical examples are polymeric fluids, heat and electric conductors at low temperature, superconductors, and so on. An accurate understanding of these systems may thus be important not only from a theoretical point of view, but also for practical purposes. In real situations, these systems are out of equilibrium. Accordingly, there is an urgent need for a non-equilibrium thermodynamic theory able, on the one hand, to cope with the effects of long relaxation times and, on the other, to complement other formalisms based on the use of internal variables.

There are other reasons for the present study. One should be aware that classical irreversible thermodynamics is not the only non-equilibrium thermodynamic theory: other theories, in particular the so-called rational thermodynamics, have achieved some valuable results. To reconcile the classical and the rational points of view, it would be of interest to have a theory able to provide a sufficiently wide ground for discussion, thus making their common points evident and their main differences understandable. Extended irreversible thermodynamics is a promising candidate.

Extended irreversible thermodynamics received a strong impetus in the past decade. Besides the classical thermodynamic variables, this theory introduces as new independent variables the dissipative fluxes and aims to obtain for them evolution equations compatible with the second law of thermodynamics. The central quantity is a generalised non-equilibrium entropy, depending on both the conserved variables and the fluxes, which sheds new light on the content of the second law. This generalised theory is corroborated from a microscopic point of view by the kinetic theory, non-equilibrium information theory and other formulations of non-equilibrium statistical mechanics.

The purpose of this book is to provide an introduction to the foundations of extended irreversible thermodynamics, to discuss the main results and to present some of its applications. After more than twenty years of research and several hundreds of papers published by many groups in several countries we feel such a book is sorely needed. Guided by the aim to be as illustrative and pedagogical as possible, a relatively simple formulation of the theory is presented, but this is nevertheless more than sufficient for the description of several phenomena not accessible to the classical theory. The various topics treated in this book range from thermal waves and phonon hydrodynamics to material and electrical transport, from ultrasound propagation and generalised hydrodynamics to rheology, from kinetic theory to cosmology. Of course, other formulations of extended thermodynamics and other kinds of applications are possible. They are likely to arise in the near future. We hope that this book will be useful in providing a general view of present achievements and in stimulating future research.

We are very pleased to acknowledge many stimulating discussions with our colleagues Carlos Pérez-García, Josep-Enric Llebot, Diego Pavón, José-Miguel Rubí and Joseph Lambermont for more than fifteen years of joint research, and also with many other colleagues from the different groups which have devoted their attention to extended irreversible thermodynamics. We also acknowledge the financial support of the Comisión Asesora para la Investigación Científica y Técnica of the Spanish Government during the years 1979–1986 under grants 3913/79 and 2389/83, and of the Dirección General de Investigación Científica y Técnica of the Spanish Ministry of Education, under grants PB86–0287, PB89–0290, and PB90–0676. The collaboration between our groups in Bellaterra and Liège has been made economically possible because of the NATO grant 0355/83.

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