# Preface

The thermodynamics of flowing fluids is an active and very challenging topic in modern non-equilibrium thermodynamics and statistical mechanics. After ten years of publication of the first edition of this book, we felt that a fully renewed, updated and enlarged edition was necessary to cover some of the progress made in these fields. A book on the thermodynamics of flowing fluids was published in 1994 by A. N. Beris and S. J. Edwards, *Thermodynamics of Flowing Fluids with Internal Microstructure*, Oxford University Press, New York, 1994: it was based on the Poisson bracket formalism and focused on fluids with internal microstructure. The books by D. J. Evans and G. P. Morriss, *Statistical Mechanics of Nonequilibrium Liquids* (Australian National University E Press, 2007), A. Onuki, *Phase Transition Dynamics* (Cambridge University Press, 2002) and V. Garzó and A. Santos, *Kinetic theory of gases in shear flow* (Kluwer, Dordrecht, 2003) have also been useful and important contributions to a global vision of this field, the first with more emphasis on molecular dynamical simulations, the second one with special attention on critical phenomena, and the third one from the perspective of the kinetic theory of gases. The central perspective of the present book is, instead, on non-equilibrium thermodynamics beyond local equilibrium. The more macroscopic and phenomenological character of this approach allows to deal with a wider range of systems, going from ideal gases and phonon hydrodynamics to polymer solutions and melts, and to laminar and turbulent superfluids.

The interest of the thermodynamics of flowing fluids is both theoretical and practical. From the theoretical point of view, the influence of the flow on the thermodynamic potentials requires the formulation of thermodynamic theories beyond the local-equilibrium hypothesis; this is a field with many open challenges, which fosters an active dialogue between macroscopic and microscopic theories, the latter based either on the kinetic theory of gases, or on molecular dynamical simulations of fluids. Furthermore, it also requires an open discussion between thermodynamics and hydrodynamics, because some of the observed phenomena may have a purely thermodynamic origin (due to the modification of some equations of state) or a purely hydrodynamic origin, but in general there will be an interplay of both thermodynamics beyond the local-equilibrium regime, and its relationship with microscopic theories and with hydrodynamic theories currently represents an important frontier of research. In our book by G. Lebon, D. Jou and J. Casas-Vázquez, *Understanding Non-equilibrium Thermodynamics. Foundations, Applications, Frontiers* (Springer, Berlin, 2008) we have discussed and examined in detail several different avenues towards the formulation of such thermodynamics beyond local equilibrium.

From the practical point of view, many situations of technological interest are present in flowing systems. Indeed, the modification of the thermodynamic equations of state for the chemical potential imply modifications in the phase diagram of substances in non-equilibrium steady states, or on the conditions of chemical equilibrium and stability. The ability to control the thermodynamic state of the system is essential in technology and also in fundamental science. For instance, much study has been devoted to flow-induced changes in the phase diagram of polymer solutions or in shear-induced flow of macromolecules. The practical importance of the problems arising under flow is easily understood. Most industrial processes take place in flowing fluids (pumping, extruding, injecting, molding, mixing…), in which the polymer macromolecules undergo different shear and elongational stresses, depending on the position. Thus, a flow-induced change of phase could take place in some positions and not in others, affecting both rheological and structural properties of the flow. The materials formed in these processes may be very sensitive to the extent of the phase transitions occurring in the fluids previous to solidification.

Other related fields of interest are the thermodynamically induced polymer degradation under flow, which may be important in viscous drag reduction, or in flows of polymer solutions through packed porous beds, as in membrane permeation or flow of oil through soil and rocks. Also, in biological experiments shear-induced precipitation and degradation of proteins has been observed, and new separation techniques have been devised on the effects of the interaction between viscous pressure and diffusion. Microfluidics and nanofluidics have experienced a strong development in the last ten years, opening new and surprising applications of flowing fluids at a minuscule scale. In particular, phonon hydrodynamics provides a useful phenomenological basis to analyze heat transport from the diffusive to the ballistic regimes, with application to nanosystems and nanowires, thin layers, tubular layers, porous superlattices and so on.

From a more fundamental point of view, some of the main experiments in nuclear and particle physics refer to the transition from nuclear hadronic to a quark-gluon plasma. This is pursued through very energetic ultrarelativistic collisions of heavy nuclei. The total duration of such collisions is of the order of five to ten times the mean time between successive collisions amongst nucleons in the nuclei. Therefore, the nuclei are rather far from local equilibrium during the collision and it is problematic to what extent an analysis based on the local-equilibrium equations of state for nuclear matter and for quark-gluon plasma and normal hydrodynamics may be sufficient to provide a reliable description of the transition. Efforts towards using more general non-equilibrium thermodynamic and hydrodynamic theories are a challenge in this field. Another topic where the flow has a deep influence on the fluids is in turbulent superfluids, where a tangle of quantized vortex filaments appears for sufficiently high values of the heat flow or of the relative velocity between normal and superfluid components. This vortex tangle contributes to the internal friction of the fluid, and it is by itself an interesting phase of matter, constituted of vortex loops and filaments. Finally, at a more abstract level, understanding the meaning and the mutual relationships between several definitions of temperature and entropy finds in flowing fluids an interesting benchmark where explicit illustrations are possible.

From a thermodynamic perspective, the already mentioned book by Beris and Edwards was based on Hamiltonian formalisms, as Poisson brackets, which has achieved a more general and elegant formulation in the so-called GENERICS, which has been presented in detail by H. C. Öttinger in the book *Beyond Equilibrium Thermodynamics* (Wiley, New York, 2005). Here, instead, we adopt extended irreversible thermodynamics as our general framework, and we try to emphasise both the general thermodynamic structure underlying fluids without internal structure (namely, ideal gases, phonons, real gases, simple fluids) as well as fluids with internal structure (namely, polymer solutions and blends, and turbulent superfluids). In this way, this volume may be seen as a complement of our monograph D. Jou, G. Lebon and J. Casas-Vázquez, *Extended Irreversible Thermodynamics* (fourth edition, Springer, Berlin, 2010), dealing with a variety of problems that were not included in that volume for the lack of space.

A decisive step in the thermodynamic understanding of flowing fluids is to formulate a free energy depending explicitly on the characteristics of the flow. This important problem in non-equilibrium thermodynamics has not yet received as much attention as it deserves. It must be noted that several authors have preferred to follow another method, to analyse the phase separation or phase homogenization under shear from a dynamical point of view, i.e. by writing dynamical equations for the behaviour of concentration and velocity fluctuations and analysing the stability of the corresponding set of equations. Of course, the dynamical procedure has a wider range of potentialities than the pure thermodynamic analysis: the latter may be able to set the spinodal line limiting the regions of stability, but it certainly cannot give a detailed view of the processes of segregation of both phases, or about the changes in viscosity observed during the segregation. However, the existence of both methods is not contradictory, e.g., the dynamical method may describe the instability through the change of sign of an effective diffusion coefficient, but this change of sign is produced at the spinodal line, and this fact is related, in many situations, to the vanishing of the first derivative of an effective chemical potential with respect to the composition. Furthermore, the dynamical analysis cannot avoid the use of equations of state of the flowing fluid; therefore, to find and analyse equations of state in non-equilibrium conditions is always of interest. Thus, although there is a common ground for thermodynamical and dynamical analyses, both methods have their own advantages and disadvantages, so that it would be unwise to dismiss a priori either of them.

Here, we give a brief description of the contents of the book, and point to the changes made with respect to the first edition. In Chap. 1, we provide the general basis from a macroscopic point of view, or more precisely from the perspective of extended irreversible thermodynamics, and we compare it with other macroscopic theories, as rational thermodynamics, theories with internal variables, and Hamiltonian theories. Chapters 2 and 3—the much enlarged outcomes of the Chap. 2 of the first edition—deal with ideal gases: in Chap. 2 we use information theory to describe the steady state of flowing ideal gases under Couette flow, and we explore in depth how several definitions of temperature behave in the presence of a non-vanishing viscous pressure, and how they relate to each other. Of course, in the absence of the viscous pressure all of them tend to the same value, identical to the local-equilibrium temperature. In Chap. 3 we remind the basic concepts of the kinetic theory description of flowing ideal gases, and we discuss with some detail the application of thermodynamic ideas to the flow of phonons in the so-called phonon hydrodynamics, with special emphasis on the application of this formalism to heat transfer in nanosystems. This requires taking into detailed consideration the boundary conditions for the slip heat flow along the walls of the system. This topic was not considered in the second edition.

Chapter 4 is devoted to non-ideal gases, with a comparison with some results of molecular dynamical simulations, and with an application to some thermodynamic and hydrodynamic aspects of relativistic ion collisions. Chapter 5 discusses the microscopic description of polymer solutions, as kinetic theory of dilute solutions, reptation model for concentrated solutions, and double-reptation model for polymer blends, to which much attention is devoted in further chapters. Chapter 6 analyzes the influence of a shear flow on the phase diagram of polymer solutions, and shear-induced phase transitions; the first edition was limited to dilute solutions whereas the present one incorporates also concentrated solutions and polymers blends. Chapter 7 considers dynamical effects, the role of hydrodynamically enhanced fluctuations, and provides an understanding of the range of application of the thermodynamic formalism. Chapters 8 and 9 enlarge the contents of Chap. 7 of the first edition. Chapter 8 deals with the couplings of viscous pressure and diffusion; in particular, much attention is devoted to shear-induced diffusion and its applications to macromolecular separation in cone-and-plate and in tube configurations. Chapter 9 is also devoted to diffusion in the presence of a velocity gradient, with special attention to Taylor dispersion and its applications, and to anomalous diffusion, both in a system at rest as in a fluid with a velocity gradient. Chapter 10 deals with chemical reactions under flow, both for ideal gases and polymer solutions; the latter case is applied to the analysis of polymer degradation due to the flow. Chapter 11 discusses the thermodynamics of flowing superfluids, not only in the well-known laminar regime, but also in the more intriguing and challenging turbulent regime, with quantized vortices. Appendix A is devoted to a survey of experimental information on the relevant material functions used for the evaluation of the non-equilibrium chemical potential in the examples considered in the book, and Appendix B briefly describes the results on the influence of a shear flow on the isotropic-nematic transition in liquid crystals. Appendices C–E contain other useful information related to mathematical results.

We acknowledge fruitful discussions on a variety of these topics with Profs. G. Lebon (Université de Liège, Belgium), M. S. Mongiovì (Università di Palermo, Italy), R. Luzzi (Universidade de Campinas, Brazil), M. Grmela (École Polytechnique de Montréal, Canada), L. F. del Castillo (Universidad Nacional Autónoma de México, México), Y. Katayama (Nihon University, Koriyama, Japan), W. Muschik (Technische Universität Berlin, Germany), H. C. Öttinger (ETH Zurich, Switzerland), V. A. Cimmelli (Università della Basilicata, Potenza, Italy), J. Camacho and V. Méndez (Universitat Autònoma de Barcelona) and J. Fort (Universitat de Girona), and with Drs F. X. Alvarez (Universitat Autònoma de Barcelona), A. Sellitto (Università della Basilicata, Potenza, Italy), and M. Sciacca (Università di Palermo, Italy). Dr V. Ortega-Cejas (Universitat Autònoma de Barcelona) has been very helpful in providing technical help for the final version of the manuscript.

This work has received the support of the Dirección General de Investigación Científica y Técnica of the Spanish Ministry of Education and Science, under grants PB90-0676, PB94-0718, FIS2006-12296-C02-01, Ministry of Science and Technology (grants BFM 2000-0351-C03-01, BFM-2003-06033), Ministry of Science and Innovation (grant FIS2009-13370-C02-01), of European Union in the framework of the Program of Human Capital and Mobility (grant ERB-CHR XCT 920 007) and of the Direcció General de Recerca of the Generalitat of Catalonia (grants 1997 SGR 00387, 1999 SGR 00095, 2001 SGR 00186, 2005 SGR 0087, 2009 SGR 164). M. Criado-Sancho acknowledges the support of the Universidad Nacional de Educación a Distancia (UNED, Madrid, Spain).

July 2010
Bellaterra, Barcelona

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http://www.springer.com/978-94-007-0198-4

Thermodynamics of Fluids Under Flow
Jou, D.; Casas-Vázquez, J.; Criado-Sancho, M.
2011, XV, 301 p., Hardcover
ISBN: 978-94-007-0198-4