

# Preface

As stated by Sybren de Groot and Peter Mazur<sup>1</sup> “Non-equilibrium thermodynamics provides us with a general framework for the macroscopic description of irreversible processes.” Its basic step is to extend the meaning of all thermodynamic properties that we typically associate with equilibrium states, so that we can define and thus apply them locally to systems out of equilibrium. It should be stressed, however, that a general theory of non-equilibrium thermodynamics can be developed only when the driving forces and the resulting fluxes (e.g. the temperature gradient and the induced diffusive heat flux) can be assumed to be linearly related to each other. This assumption is satisfied when the driving forces are not very strong and when their time rates of change are not very fast, so that the entire system does not deviate substantially from its equilibrium state. Although the assumption of linear force-flux relations seems very limiting, though, in reality it applies very well to most cases. Think, for example, to the laws of Fick, Fourier and Newton, relating the diffusive fluxes of mass, heat and momentum to their respective driving forces, i.e. the gradients of chemical potential, temperature and velocity: these relations appear to apply very well even to systems far from equilibrium, i.e. when the driving forces are not small. In any case, we do not have to forget that the general case of far from equilibrium systems is heavily non-linear and can only be tackled using non-equilibrium statistical mechanics.

This book is divided into two parts. The first part presents the theory of non-equilibrium thermodynamics, reviewing its essential features and showing, when possible, some applications. After describing in Chap. 1 the local equilibrium assumption and the theory of fluctuations, in Chap. 2 we derive the celebrated Onsager’s reciprocity relations and the fluctuation-dissipation theorem. Then, in Chaps. 3 and 4, we describe the most common ways to follow the evolution of stochastic systems, namely the Langevin and the Fokker-Planck equations. Chapters 5 and 6 are more advanced, as they describe alternative ways to study the trajectories of random systems, namely stochastic integration and path integrals.

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<sup>1</sup>S.R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics*, Dover (1962).

In the second part of this book, we show how the general theory of non-equilibrium thermodynamics can be applied to model multiphase flows and, in particular, to determine their constitutive relations. After deriving all balance equations in Chap. 7, in Chap. 8 we apply the results of non-equilibrium thermodynamics to derive the constitutive relations. Then, in Chap. 9, we describe the diffuse interface model of multiphase flows, as it is more fundamental than the classical, sharp interface theory and is therefore more suitable to be coupled to all non-equilibrium thermodynamics results. Finally, Chaps. 10 and 11 are devoted to determining the effective constitutive relations and the effective equations of complex fluids and composite materials. At the end, several appendices deal with some prerequisite topics in mathematics, statistical thermodynamics, analytical mechanics and transport phenomena.

This book grew out of graduate lectures on non-equilibrium thermodynamics which I have given at the City College of New York and at the University of Pisa to students of engineering and material science. No prior knowledge of statistical mechanics is required; the necessary prerequisites are only the equivalents of an introductory course on transport phenomena and one on thermodynamics.

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