

*Beyond Equilibrium
Thermodynamics*

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Preface

The Credo of Coarse-Graining

“Everything should be made as simple as possible, but not simpler.”
Albert Einstein¹

“It’s too early to write such a book,” was my standard reply to colleagues who asked me when I would finally write a book on modern nonequilibrium thermodynamics. I’m afraid that this answer is still true, even today, on September 23, 2004. Therefore, what you have in your hands should not be considered as a regular or final book. Rather it is the beginning of a project, the maybe premature birth of a textbook–encyclopedia–research guide *chimera*, a vivid vision to be materialized in forthcoming decades. The title of the project, “Beyond Equilibrium Thermodynamics,” is meant to indicate that its horizon extends far beyond the well-established regimes of equilibrium and linear irreversible thermodynamics; I hope that the book-like object in your hands will actually help to shape a new paradigm of “beyond-equilibrium thermodynamics,” useful to solve many existing problems and to identify even more interesting new ones, providing powerful methods and a unified language encompassing and clarifying all the competing previous formulations of nonequilibrium thermodynamics.

In my attempt at painting a balanced picture of beyond-equilibrium thermodynamics, several new problems have already been identified and solved. For example, the treatment of redundant variables in Section 1.2.1, the thermodynamically admissible

¹ According to Reader’s Digest (October 1977).

incorporation of diffusion into the Navier-Stokes equations in Section 2.2.5, the formulation of linear response theory within the unified framework in Section 6.2.3, the thermodynamically admissible kinetic theory of gases in Section 7.4.3, the thermodynamically guided analysis of molecular dynamics simulations of entangled polymers in Section 8.4.6, and the geometric derivation of Poisson brackets for configurational distribution functions in Appendix B.4 are all original contributions, published for the first time. Some of the earlier developments stimulated by this project have been published in separate papers.

Over the past four decades, the phenomenological theory of irreversible processes has matured from a collection of linear constitutive laws and phenomenological balance equations into a robust, systematic, and practical methodology to treat nonequilibrium systems. However, the methods of statistical mechanics, in particular well-founded simulation techniques, need to be further developed into a powerful tool for engineering applications. Among the basic problems awaiting further clarification, boundary conditions and open systems are prominent examples, and a unified approach to nonequilibrium systems should cover rare jumps in addition to the continuous dynamics of slow variables.

Nonequilibrium thermodynamics is the key to *understanding* time-dependent phenomena. In order to appreciate such a bold statement one should realize that there are different concepts of “understanding.” On the one hand, one can argue that a deep understanding of nature should be achieved through a consistent theory of all fundamental particles and interactions. On the other hand, understanding certain phenomena is more often regarded as the art of distilling the essence of the phenomena, that is, describing them in as simple terms as possible, with as few variables as absolutely necessary. For example, clearly an “understanding of turbulence” has nothing to do with fundamental particles; what is one really looking for in view of the fact that the Navier-Stokes equation can probably reproduce all the observed phenomena of turbulence? After sketching four different approaches to the scientific study of turbulence, Kadanoff states that,² “In each case, we are trying to isolate elements of the flow that are open to prediction, replication, and comparison among different systems.” The process of understanding can be regarded as the search for the coarsest possible description of a phenomenon, and nonequilibrium thermodynamics, as the theory of coarse-graining, is hence a cornerstone for understanding the essence of time-dependent phenomena. It should therefore be useful to present a unified theory of coarse-grained systems and the procedure of coarse-graining as the road to understanding through simplicity. Thermodynamics provides the road, and one should not be disappointed that one still needs the vehicle of creative ideas for progressing along that road.

While linear irreversible thermodynamics was fully developed in the mid-20th century, a unified formulation of nonlinear nonequilibrium thermodynamics is clearly needed. Most complex fluids processed in various industries exhibit highly nonlinear material behavior, and progress in the understanding of soft condensed matter is linked

²Kadanoff, *Physics Today* 54/8 (2001) 34.

to new developments in thermodynamics. As “*nonlinear nonequilibrium*” sounds too negative, we here refer to the unified new approach to nonequilibrium phenomena with an emphasis on the nonlinear regime as “*beyond-equilibrium thermodynamics*.” This new term sounds more positive and nicely emphasizes the important message that constructive tools are now available for systems far away from equilibrium. These tools should be useful to many scientists and engineers, and my goal hence is to address the curiosity of theoretical physicists as much as the needs of chemical engineers.

Among the classical subjects of nonequilibrium thermodynamics, balance equations, hydrodynamics, the local-equilibrium assumption, the linear thermodynamics of irreversible processes, the Onsager-Casimir relationships, projection-operator techniques, Boltzmann’s kinetic equation, linear response theory and the fluctuation-dissipation theorems of the first and second kind are covered extensively in the unified approach followed here. The Chapman-Enskog method and Grad’s moment expansion, as important tools to solve equations, are discussed, too. On the other hand, classical topics like the BBGKY hierarchy lose their importance in the new approach to beyond-equilibrium thermodynamics and are hence only mentioned in passing.

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