

Chapter 1

Scope

The aim of this book is to present a systematic theory of transport for heterogeneous systems. The theory is an extension of non-equilibrium thermodynamics for transport in homogeneous phases, a field that was established in 1931 and developed during the nineteen forties and fifties. The foundation to describe transports across surfaces in a systematic way was laid in the nineteen eighties. In this chapter, we put the theory in context and give perspectives on its application.

1.1 What is non-equilibrium thermodynamics?

Non-equilibrium thermodynamics describes transport processes in systems that are out of global equilibrium. The field resulted from the work of many scientists with the overriding aim to find a more useful formulation of the second law of thermodynamics in such systems. The effort started in 1856 with Thomson's studies of thermoelectricity [7]. Onsager however, is counted as the founder of the field with his papers from 1931 [8,9], see also his collected works [10], because he put earlier research by Thomson, Boltzmann, Nernst, Duhem, Jauman and Einstein into the proper perspective. Onsager was given the Nobel prize in chemistry in 1968 for these works.

In non-equilibrium thermodynamics, the second law is reformulated in terms of the local entropy production in the system, σ , using the assumption of local equilibrium (see Sec. 3.5). The entropy production is given by the product sum of so-called conjugate fluxes, J_i , and forces, X_i , in the system. The second law becomes

$$\sigma = \sum_i J_i X_i \geq 0 \quad (1.1)$$

Each flux is a linear combination of all forces,

$$J_i = \sum_j L_{ij} X_j \quad (1.2)$$

The reciprocal relations

$$L_{ji} = L_{ij} \quad (1.3)$$

were proven for independent forces and fluxes, cf. Chapter 7 by Onsager [8,9]. They now bear his name. All coefficients are essential, as explained in Chapter 2. In order to use non-equilibrium thermodynamics, one first has to identify the complete set of extensive, independent variables, A_i . We shall do that in Chapters 4–6 for homogeneous phases, surfaces and three phase contact lines respectively. The conjugate fluxes and forces are

$$J_i = dA_i/dt \quad \text{and} \quad X_i = \partial S/\partial A_i \quad (1.4)$$

Here t is the time and S is the entropy of the system. Some authors have erroneously stated that any set of fluxes and forces that fulfil (1.1) also obeys (1.3). This is not correct. We also need Eq. (1.4). Equations (1.1) to (1.4) contain all information on the non-equilibrium behavior of the system.

Following Onsager, a systematic theory of non-equilibrium processes was set up in the nineteen forties by Meixner [11–14] and Prigogine [15]. They found the rate of entropy production for a number of physical problems. Prigogine received the Nobel prize in 1977 for his work on the structure of systems that are not in equilibrium (dissipative structures), and Mitchell the year after for his application of the driving force concept to transport processes in biology [16].

Short and essential books were written early by Denbigh [17] and Prigogine [18]. The most general description of classical non-equilibrium thermodynamics is still the 1962 monograph of de Groot and Mazur [19], reprinted in 1985 [20]. Haase's book [21], also reprinted [22], contains many experimental results for systems in temperature gradients. Katchalsky and Curran developed the theory for biological systems [23]. Their analysis was carried further by Caplan and Essig [24], and Westerhoff and van Dam [25]. Førlund and coworkers' book gave various applications in electrochemistry, in biology and geology [26]. This book, which presents the theory in a way suitable for chemists, has also been reprinted [27]. A simple introduction to non-equilibrium thermodynamics for engineers is given by Kjelstrup, Bedeaux and Johannessen [28,29].

Non-equilibrium thermodynamics is all the time being applied in new directions. Fitts showed how to include viscous phenomena [30]. Kuiken [31] gave a general treatment of multicomponent diffusion and rheology of colloidal and other systems. Kinetic theory has been central for studies of evaporation [32–35], and we shall make a link between this theory and non-equilibrium thermodynamics [36–40] (see Chapter 11). A detailed discussion of the link between kinetic theory and non-equilibrium thermodynamics was made by Roldughin and Zhdanov [41]. The relation to the Maxwell–Stefan equations are given in Chapter 12, following Kuiken [31] and Krishna and Wesselingh [42]. Bedeaux and Mazur [43] extended non-equilibrium thermodynamics to quantum mechanical systems. All these efforts have together broadened the scope of non-equilibrium thermodynamics, so that it now appears as a versatile and strong tool for the general description of transport phenomena.

All the applications of non-equilibrium thermodynamics mentioned above use the linear relation between the fluxes and the forces given in Eq. (1.2). For chemical reactions the rate is given by the law of mass action, which is a nonlinear function of the driving force. This excludes a large class of important phenomena from a systematic treatment in terms of classical non-equilibrium thermodynamics. Much effort has therefore been devoted to solve this problem, see [44] for an overview. A promising effort seems to be to expand the variable set by including variables that are relevant for the mesoscopic level. The description on the mesoscopic level can afterwards be integrated to the macroscopic level. This was first done by Prigogine and Mazur, see the monograph by de Groot and Mazur [20], but Rubi and coworkers have pioneered the effort since then [45–47]. In this manner it has been possible to describe activated processes like nucleation [48]. Results compatible with results from kinetic theory [49] were derived [50], and a common thermodynamic basis was given to the Nernst and Butler–Volmer equations [51]. The systematic theory was also extended to active transport in biology [52, 53] and to describe single RNA unfolding experiments [54]. This theoretical branch, called *mesoscopic* non-equilibrium thermodynamics, is however outside the scope of the present book.

Newer books on equilibrium thermodynamics or statistical thermodynamics often include chapters on non-equilibrium thermodynamics, see e.g. [55]. In 1998 Kondepudi and Prigogine [56] presented an integrated approach to equilibrium and non-equilibrium thermodynamics. Öttinger addressed the non-linear regime in his book [57]. An excellent overview of the various extensions of non-equilibrium thermodynamic was given by Muschik *et al.* [44].

1.2 Non-equilibrium thermodynamics in the context of other theories

Non-equilibrium thermodynamics is a theory describing transport on a macroscopic level. Let us compare theories of transport on the particle level, the mesoscopic level, and the macroscopic level. Consider first equilibrium systems on all three levels, see Fig. 1.1. Classical mechanics and quantum mechanics describe the system on the particle level. Statistical mechanics provides the link from the particle level to both the mesoscopic level and the macroscopic level (indicated by arrows in the figure). The mesoscopic level describes the system on an intermediate time and length scale. Equilibrium correlation functions are calculated at this level. The macroscopic level is described by equilibrium thermodynamics, see Chapter 3 in this book. Many of these macroscopic properties can be calculated as integrals over equilibrium correlation functions. The same quantities can also be calculated using ensemble theory.

The description of non-equilibrium systems can be illustrated similarly, see Fig. 1.2. On the particle level, the time-dependence is again described by classical and quantum mechanics, while non-equilibrium statistical mechanics provides the link between this level and the mesoscopic and macroscopic levels. Theories for the particle- and mesoscopic level make it possible to calculate macroscopic transport coefficients. They use expressions for transport coefficients as integrals over equilibrium correlation functions of the fluxes, the Kubo relations. Transport coefficients can also be calculated using non-equilibrium statistical mechanics. The macroscopic level is now described by non-equilibrium thermodynamics. The present book is devoted to this description on the general level (Chapters 7–10) and in many applications (Chapters 11–23).

1.3 The purpose of this book

Most references mentioned above concern transport in homogeneous systems. It is known, however, that much entropy is produced at surfaces between homogeneous phases [41, 58], and the nature of the equations of transport for this region is also unexplored in many ways.

The aim of the present book is to further develop the theory of non-equilibrium thermodynamics to *transport in heterogeneous systems*. The foundation for the work was laid by Bedeaux, Albano and Mazur [2, 3], see also Bertrand and Prud'homme [59, 60] and a review by Bedeaux [4]. We gave a short overview of the objectives and the methods used in [61].

Heterogeneous systems distinguish themselves from homogeneous systems by their inclusion of interfaces, or phase boundaries. The interface

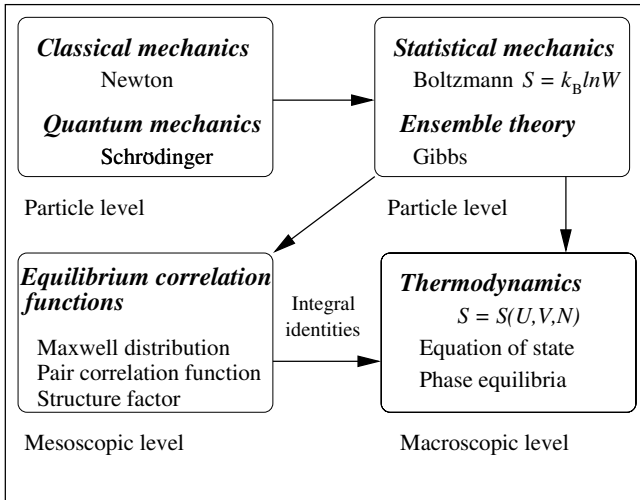


Figure 1.1 Theories for equilibrium systems on the particle-, mesoscopic- and macroscopic level.

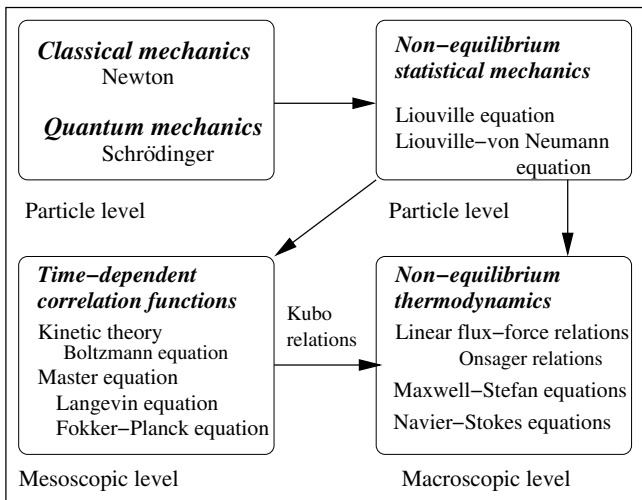


Figure 1.2 Theories for non-equilibrium systems on the particle-, mesoscopic- and macroscopic level.

can, according to Gibbs [62], be regarded as a separate two-dimensional thermodynamic system within the larger three-dimensional system. This implies the introduction of excess densities along the surface. *The purpose of this book is to extend the work of Gibbs to non-equilibrium systems.* This implies the introduction of not only time dependent excess densities for the surface but also of time dependent excess fluxes along the surface. In this manner we shall describe transport of heat, mass and charge and chemical reactions in heterogeneous systems.

Isotropic homogeneous systems have no coupling between vectorial phenomena (transport of heat, mass and charge) and scalar phenomena (chemical reactions). In these systems, the two classes can therefore be dealt with separately [20]. In a two-dimensional surface, all transport processes in the direction normal to the surface become scalar. This means that coupling can occur between transport of heat, mass and charge in that direction, and chemical reactions. The coupling is typical for electrode surfaces, phase transitions and membrane surfaces, and the coupling coefficients are often large. This coupling is special for heterogeneous systems, and is studied in many examples throughout the book. The flux equations at the surfaces give jumps in intensive variables, and define in this manner boundary conditions for integration through the surface. Such integrations can be found in several chapters. Electric potential changes shall be described by a change in the electromotive force, or in the electrochemical potential difference of the ion, which is reversible to the electrode pair [23, 27, 63].

With a short exception for the contact line (Chapter 6), we shall not consider transport along the surface. While this is an extremely important phenomenon, it would be too much new material to cover. We further neglect viscous phenomena. We shall not deal with systems where it is necessary to take fluxes along as variables [64]. We shall not introduce internal variables [45–47]. The transports considered in this book are almost all in the direction normal to the surface, and are therefore one-dimensional.

The book aims to make clear that non-equilibrium thermodynamics is a systematic theory that rests on sound assumptions. The assumption of local equilibrium is valid for systems in large gradients [65, 66], including surfaces [40, 67, 68], and does *not* depend on stationary state conditions, constant external forces, absence of electric polarization or isotropy, as has been claimed, see for instance [22].