Energy 219 (2021) 119601

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Book review

Title:	**Non-equilibrium thermodynamics of heterogeneous systems**
Author(s):	**Signe Kjelstrup, Dick Bedeaux**
Edition:	**2nd Edition**
Number of Pages:	**473**
ISBN:	**978-981-121-676-3**

This book extends non-equilibrium thermodynamics to heterogeneous systems, specifically to systems consisting of two homogeneous phases separated by a phase boundary referred to as surface or interface. In this extension the homogeneous phases and the phase boundary are treated as separate thermodynamic systems with the assumption that each one satisfies local equilibrium. The book focusses on transport of mass, heat, and charge in the direction perpendicular to the phase boundary. In isotropic homogeneous systems there is no coupling between vectorial transport phenomena like transport of mass, heat, or charge, and scalar phenomena like chemical reactions. In two-dimensional surfaces or interfaces all transport processes in the direction normal to the interface become scalar. The book gives a systematic treatment of the resulting couplings between transport of mass, heat, and charge and chemical reactions in heterogeneous systems. The consequences of these couplings are profound as elucidated for many processes like evaporation and condensation, mass diffusion, heat diffusion and cross effects, and for a variety of applications involving transfer of chemical and electrical energy. The book does not consider convective or viscous phenomena. While convection and shear flow will disturb chemical reactions and transport of heat and mass, they do not couple to these directly, so that these effects can be treated without a need for introducing new concepts in non-equilibrium thermodynamics.

After two introductory chapters describing some basic features of non-equilibrium thermodynamics and the purpose of the book, the authors review the relevant equations of equilibrium thermodynamics for the two homogeneous phases and the separating surface, first in global equilibrium and subsequently in local equilibrium. including the concept of excess surface thermodynamic properties. They then proceed to review entropy production in the homogeneous phases from traditional non-equilibrium thermodynamics. The new material starts in Chapter 5 with a description of the excess entropy production for the surface, followed by an interlude on the excess entropy production for a three-phase contact line in Chapter 6. Chapter 7 gives the general form of the flux equations and the Onsager relations that result from the expression for the entropy production. The following Chapters 8 to 12 deal with transport of heat and mass in heterogenous systems, transport of heat and mass with some thermoelectric applications, transport of mass and charge in electrochemical cells, evaporation and condensation in one-component fluids, multicomponent diffusion and heats of transfer in heterogeneous systems, respectively. Chapters 13 till 17 describe a number of additional electrochemical applications, including non-isothermal concentration cells, electrochemical cells, adiabatic electrode reactions, liquid junction potential between two aqueous electrolytes, and conversion of chemical into electrical energy in formation cells. Chapter 18 describes transport of heat and mass across membranes in osmosis, Chapter 19 deals with heterogeneous polymer electrolyte fuel cells, Chapter 20 with transport in cation-exchange membranes, and Chapter 21 with the impedance of an electrode surface. In Chapter 22 the authors review results of non-equilibrium molecular dynamics simulations verifying the assumption of local equilibrium and the validity of Onsager relations. Chapter 23 is an interesting chapter extending the square gradient theory of van der Waals for the vapor-liquid interface to non-equilibrium.

The present book is an update of the first edition that was earlier published in 2008. The chapters discussed above are identical to those in the first edition. These chapters all deal with transport phenomena across flat surfaces. In the new edition of the book the authors have added a chapter extending the non-equilibrium square gradient theory to curved vapor-liquid interfaces in liquid droplets and vapor bubbles. After reviewing the known curvature dependence of the surface tension, they show how the non-equilibrium resistivities, in contrast to those of flat interfaces, also depend on the curvature. Another new chapter shows how the surface temperature of a heterogeneous catalyst differs from the temperature of the adjacent phases using the example of oxidation of carbon monoxide to carbon dioxide on a platinum surface as a catalyst. An interesting conclusion is that a nonlinear Arrhenius plot as a function of the inverse gas temperature becomes linear when the gas temperature is replaced with the surface temperature. In the new edition, the authors have also dropped the separation of labeling Chapters 4 to 10 as “General Theory” and the remaining chapters as “Applications”. And indeed, several of the later chapters also contain very important aspects of general theory, such as Chapter 12 on the relation between multi-component diffusion and Maxwell-Stephan diffusion coefficients, and Chapters 23 and 24 on the non-equilibrium square gradient theory for the vapor-liquid interface.

The authors of the book are recognized experts in non-equilibrium thermodynamics. They give a very scholarly treatment of the concepts needed for dealing with transport phenomena across surfaces and interfaces. They also explain the relationship of their treatment of non-equilibrium thermodynamics with the

https://doi.org/10.1016/j.energy.2020.119601

literature. For instance, they discuss carefully the difference between entropy production and the concept of dissipation function employed by others in non-equilibrium thermodynamics. They show that entropy production should be the basis of non-equilibrium thermodynamics. They also provide evidence for some basic assumptions like local thermodynamic equilibrium and of the validity of the Onsager relations, not only for homogeneous phases, but also for the vapor-liquid interface as an illustrative example. The authors also say explicitly what is not covered in the book, like surfaces that are not homogeneous along the surface. Nor do they consider mesoscopic non-equilibrium thermodynamics with internal variables, a new frontier area in non-equilibrium thermodynamics bridging kinetic theory and non-equilibrium thermodynamics in systems involving chemical reactions. The clarity of the book is admirable.

The authors say that the book is intended for a graduate-level course for physics, chemists, and engineers. And indeed, many detailed exercises help a motivated reader to really become familiar with the subject. However, the book is much more. It is a superb reference for anybody interested in the treatment of diffusional, thermal, chemical and electrical forces into or across surfaces.

Declaration of competing interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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12 December 2020
Available online 23 December 2020