Non-Equilibrium Thermodynamics of Heterogeneous Systems

SERIES ON ADVANCES IN STATISTICAL MECHANICS*

Editor-in-Chief: M. Rasetti (*Politecnico di Torino, Italy*)

Published

- Vol. 6: New Problems, Methods and Techniques in Quantum Field Theory and Statistical Mechanics
edited by M. Rasetti
- Vol. 7: The Hubbard Model – Recent Results
edited by M. Rasetti
- Vol. 8: Statistical Thermodynamics and Stochastic Theory of Nonlinear Systems Far From Equilibrium
by W. Ebeling & L. Schimansky-Geier
- Vol. 9: Disorder and Competition in Soluble Lattice Models
by W. F. Wreszinski & S. R. A. Salinas
- Vol. 10: An Introduction to Stochastic Processes and Nonequilibrium Statistical Physics
by H. S. Wio
- Vol. 12: Quantum Many-Body Systems in One Dimension
by Zachary N. C. Ha
- Vol. 13: Exactly Soluble Models in Statistical Mechanics: Historical Perspectives and Current Status
edited by C. King & F. Y. Wu
- Vol. 14: Statistical Physics on the Eve of the 21st Century: In Honour of J. B. McGuire on the Occasion of his 65th Birthday
edited by M. T. Batchelor & L. T. Wille
- Vol. 15: Lattice Statistics and Mathematical Physics: Festschrift Dedicated to Professor Fa-Yueh Wu on the Occasion of his 70th Birthday
edited by J. H. H. Perk & M.-L. Ge
- Vol. 16: Non-Equilibrium Thermodynamics of Heterogeneous Systems
by S. Kjelstrup & D. Bedeaux

*For the complete list of titles in this series, please go to
http://www.worldscibooks.com/series/sasm_series

Series on Advances in Statistical Mechanics – Volume 16

Non-Equilibrium Thermodynamics of Heterogeneous Systems

S I G N E K J E L S T R U P

D I C K B E D E A U X

Norwegian University of Science and Technology

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Series on Advances in Statistical Mechanics – Vol. 16

NON-EQUILIBRIUM THERMODYNAMICS OF HETEROGENEOUS SYSTEMS

Copyright © 2008 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN-13 978-981-277-913-7

ISBN-10 981-277-913-2

Printed in Singapore.

We dedicate this book to our teacher and friend Peter Mazur

This page intentionally left blank

Preface

What the book is about

This book describes transport through complex, heterogeneous media. There are large coupling effects between transports of heat, mass, charge and chemical reactions in such media, and it is important to know how one should properly integrate across heterogeneous systems where different phases are in contact. Transports perpendicular to planar interfaces are treated.

How we were inspired to write it

Waldmann [1] was the first to point out that an analysis of boundary conditions should be incorporated in the framework of non-equilibrium thermodynamics. He did not include excess densities to describe the properties of the surface, however. In the 1970s and 1980s Bedeaux, Albano and Mazur [2–4] extended his work and laid the theoretical foundation for the description of non-equilibrium processes, including a full description of the thermodynamic properties of the surface. The work of Bedeaux, Albano and Mazur addressed not only transports into and through a surface, but also transports along surfaces as well as the motion of the surface itself. Their methods were inspired by concurrent work on the optical properties of surfaces by Bedeaux and Vlieger [5, 6], using generalized functions for the description of surface properties. The present work takes advantage of these methodologies.

Who it is meant for

The purpose of this book is to encourage the use of non-equilibrium thermodynamics to describe transport in complex, heterogeneous media. The book is written for a graduate level course for physicists, physical chemists, chemical or mechanical engineers. The book requires knowledge of basic thermodynamics corresponding to that given by Atkins, Physical

Chemistry (Oxford University Press), or Moran and Shapiro, Fundamentals of Engineering Thermodynamics (John Wiley & Sons).

Acknowledgments

A course on non-equilibrium thermodynamics has been taught at the Norwegian University of Science and Technology for many years. We are grateful to the graduate students who worked with us on related subjects and commented on preliminary versions of the text. In alphabetical order, we would like to mention Odne Stokke Burheim, Belinda Flem, Andreas Grimstvedt, Kirill Glavatskiy, Ellen Marie Hansen, Torleif Holt, Isabella Inzoli, Eivind Johannessen, Einar Eng Johnsen, Gelein de Koeijer, Lars Nummedal, Anne-Kristine Meland, Steffen Møller-Holst, Magnar Ottøy, Audun Røsjorde, Erik Sauar, Kristin Syverud, Preben Joakim Svela Vie, Jing Xu and Anita Zvolinschi. Discussions and collaborations with colleagues Bjørn Hafskjold, Jean-Marc Simon, Fernando Bresme and Edgar Blokhuis were appreciated.

During our peaceful and inspiring stay in Kyoto University in 2000, a large step forward was made. We are grateful to our host Prof. Yasuhiko Ito, and to coworkers, Profs. Yoichi Tomii, Yasuhiro Fukunaka, Drs. Toshiyuki Nohira and Koji Amezawa. The next large step was made in beautiful Barcelona in 2004, with our considerate host, Prof. Miguel Rubi of University of Barcelona.

We thank the Research Council of Norway for financial support over many years. Marian Palcut contributed the cover image, while Tharald Tharaldsen, Jaques van der Ploeg and Michel Uiterwijk contributed many figures.

Signe Kjelstrup* and Dick Bedeaux

March 2008

Address for correspondence:

Department of Chemistry,
Norwegian University of Science and Technology,
NO-7491 Trondheim, Norway

*The author changed her name from Ratkje to Kjelstrup in 1996.

Contents

Preface	vii
1 Scope	1
1.1 What is non-equilibrium thermodynamics?	1
1.2 Non-equilibrium thermodynamics in the context of other theories	4
1.3 The purpose of this book	4
2 Why Non-Equilibrium Thermodynamics?	7
2.1 Simple flux equations	8
2.2 Flux equations with coupling terms	9
2.3 Experimental designs and controls	11
2.4 Entropy production, work and lost work	12
2.5 Consistent thermodynamic models	14
3 Thermodynamic Relations for Heterogeneous Systems	17
3.1 Two homogeneous phases separated by a surface in global equilibrium	18
3.2 The contact line in global equilibrium	22
3.3 Defining thermodynamic variables for the surface	23
3.4 Local thermodynamic identities	29
3.5 Defining local equilibrium	32
3.A Appendix: Partial molar properties	35
3.A.1 Homogeneous phases	36
3.A.2 The surface	38
3.A.3 The standard state	40
Part A: General Theory	45
4 The Entropy Production for a Homogeneous Phase	47
4.1 Balance equations	49
4.2 The entropy production	51

4.2.1	Why one should not use the dissipation function	56
4.2.2	States with minimum entropy production	57
4.3	Examples	58
4.4	Frames of reference for fluxes in homogeneous systems	64
4.4.1	Definitions of frames of reference	64
4.4.2	Transformations between the frames of reference	66
4.A	Appendix: The first law and the heat flux	67
5	The Excess Entropy Production for the Surface	73
5.1	The discrete nature of the surface	74
5.2	The behavior of the electric fields and potential through the surface	75
5.3	Balance equations	77
5.4	The excess entropy production	79
5.4.1	Reversible processes at the interface and the Nernst equation	84
5.4.2	The surface potential jump at the hydrogen electrode	86
5.5	Examples	87
6	The Excess Entropy Production for a Three Phase Contact Line	91
6.1	The discrete nature of the contact line	92
6.2	Balance equations	94
6.3	The excess entropy production	95
6.4	Stationary states	96
6.5	Concluding comment	97
7	Flux Equations and Onsager Relations	99
7.1	Flux-force relations	99
7.2	Onsager's reciprocal relations	100
7.3	Relaxation to equilibrium. Consequences of violating Onsager relations	104
7.4	Force-flux relations	105
7.5	Coefficient bounds	106
7.6	The Curie principle applied to surfaces and contact lines	108
8	Transport of Heat and Mass	111
8.1	The homogeneous phases	112
8.2	Coefficient values for homogeneous phases	114
8.3	The surface	117
8.3.1	Heats of transfer for the surface	119

8.4	Solution for the heterogeneous system	122
8.5	Scaling relations between surface and bulk resistivities . .	125
9	Transport of Heat and Charge	127
9.1	The homogeneous phases	128
9.2	The surface	130
9.3	Thermoelectric coolers	132
9.4	Thermoelectric generators	133
9.5	Solution for the heterogeneous system	135
10	Transport of Mass and Charge	139
10.1	The electrolyte	140
10.2	The electrode surfaces	143
10.3	Solution for the heterogeneous system	146
10.4	A salt power plant	147
10.5	Electric power from volume flow	148
10.6	Ionic mobility model for the electrolyte	150
10.7	Ionic and electronic model for the surface	154
Part B:	Applications	155
11	Evaporation and Condensation	157
11.1	Evaporation and condensation in a pure fluid	158
11.1.1	The entropy production and the flux equations . .	158
11.1.2	Interface resistivities from kinetic theory	165
11.2	The sign of the heats of transfer of the surface	167
11.3	Coefficients from molecular dynamics simulations	169
11.4	Evaporation and condensation in a two-component fluid .	176
11.4.1	The entropy production and the flux equations . .	176
11.4.2	Interface resistivities from kinetic theory	179
12	Multi-Component Heat and Mass Diffusion	183
12.1	The homogeneous phases	184
12.2	The Maxwell–Stefan equations for multi-component diffusion	186
12.3	The Maxwell–Stefan equations for the surface	188
12.4	Multi-component diffusion	192
12.4.1	Prigogine’s theorem	192
12.4.2	Diffusion in the solvent frame of reference	193
12.4.3	Other frames of reference	195
12.4.4	An example: Kinetic demixing of oxides	200

12.5	A relation between the heats of transfer and the enthalpy	202
13	A Nonisothermal Concentration Cell	205
13.1	The homogeneous phases	207
13.1.1	Entropy production and flux equations for the anode	207
13.1.2	Position dependent transport coefficients	210
13.1.3	The profiles of the homogeneous anode	211
13.1.4	Contributions from the cathode	212
13.1.5	The electrolyte contribution	213
13.2	Surface contributions	214
13.2.1	The anode surface	214
13.2.2	The cathode surface	217
13.3	The thermoelectric potential	218
14	The Transported Entropy	221
14.1	The Seebeck coefficient of cell a	222
14.2	The transported entropy of Pb^{2+} in cell a	226
14.3	The transported entropy of the cation in cell b	227
14.4	The transported entropy of the ions cell c	228
14.5	Transformation properties	230
14.6	Concluding comments	232
15	Adiabatic Electrode Reactions	235
15.1	The homogeneous phases	236
15.1.1	The silver phases	236
15.1.2	The silver chloride phases	236
15.1.3	The electrolyte	237
15.2	The interfaces	237
15.2.1	The silver-silver chloride interfaces	237
15.2.2	The silver chloride-electrolyte interfaces	239
15.3	Temperature and electric potential profiles	240
16	The Liquid Junction Potential	249
16.1	The flux equations for the electrolyte	250
16.2	The liquid junction potential	253
16.3	Liquid junction potential calculations compared	255
16.4	Concluding comments	258

17 The Formation Cell	261
17.1 The isothermal cell	263
17.1.1 The electromotive force	263
17.1.2 The transference coefficient of the salt in the electrolyte	263
17.1.3 An electrolyte with a salt concentration gradient .	265
17.1.4 The Planck potential derived from ionic fluxes and forces	267
17.2 A non-isothermal cell with a non-uniform electrolyte . . .	268
17.2.1 The homogeneous anode phase	269
17.2.2 The electrolyte	270
17.2.3 The surface of the anode	272
17.2.4 The homogeneous phases and the surface of the cathode	273
17.2.5 The cell potential	275
17.3 Concluding comments	275
18 Power from Regular and Thermal Osmosis	277
18.1 The potential work of a salt power plant	277
18.2 The membrane as a barrier to transport of heat and mass	279
18.3 Membrane transport of heat and mass	281
18.4 Osmosis	283
18.5 Thermal osmosis	285
19 Modeling the Polymer Electrolyte Fuel Cell	289
19.1 The potential work of a fuel cell	290
19.2 The cell and its five subsystems	291
19.3 The electrode backing and the membrane	293
19.3.1 The entropy production in the homogeneous phases	293
19.3.2 The anode backing	295
19.3.3 The membrane	298
19.3.4 The cathode backing	300
19.4 The electrode surfaces	301
19.4.1 The anode catalyst surface	304
19.4.2 The cathode catalyst surface	306
19.5 A model in agreement with the second law	307
19.6 Concluding comments	310

20 Measuring Membrane Transport Properties	311
20.1 The membrane in equilibrium with electrolyte solutions . .	312
20.2 The membrane resistivity	312
20.3 Ionic transport numbers	316
20.4 The transference number of water and the water permeability	319
20.5 The Seebeck coefficient	322
20.6 Interdiffusion coefficients	323
21 The Impedance of an Electrode Surface	327
21.1 The hydrogen electrode. Mass balances	328
21.2 The oscillating field	331
21.3 Reaction Gibbs energies	332
21.4 The electrode surface impedance	332
21.4.1 The adsorption-diffusion layer in front of the catalyst	332
21.4.2 The charge transfer reaction	336
21.4.3 The impedance spectrum	337
21.5 A test of the model	338
21.6 The reaction overpotential	339
22 Non-Equilibrium Molecular Dynamics Simulations	341
22.1 The system	344
22.1.1 The interaction potential	346
22.2 Calculation techniques	347
22.3 Verifying the assumption of local equilibrium	351
22.3.1 Local equilibrium in a homogeneous binary mixture	351
22.3.2 Local equilibrium in a gas-liquid interface	353
22.4 Verifications of the Onsager relations	356
22.4.1 A homogeneous binary mixture	356
22.4.2 A gas-liquid interface	358
22.5 Linearity of the flux-force relations	359
22.6 Molecular mechanisms	359
23 The Non-Equilibrium Two-Phase van der Waals Model	361
23.1 Van der Waals equation of states	363
23.2 Van der Waals square gradient model for the interfacial region	366
23.3 Balance equations	369
23.4 The entropy production	371
23.5 Flux equations	372

23.6	A numerical solution method	373
23.7	Procedure for extrapolation of bulk densities and fluxes . .	376
23.8	Defining excess densities	378
23.9	Thermodynamic properties of Gibbs' surface	379
23.10	An autonomous surface	380
23.11	Excess densities depend on the choice of dividing surface .	384
23.11.1	Properties of dividing surfaces	384
23.11.2	Surface excess densities for two dividing surfaces	385
23.11.3	The surface temperature from excess density differences	386
23.12	The entropy balance and the excess entropy production . .	388
23.13	Resistivities to heat and mass transfer	390
23.14	Concluding comments	392

References	393
-------------------	------------

Symbol Lists	415
---------------------	------------

Index	423
--------------	------------

About the Authors	433
--------------------------	------------