Contents

1 Introduction **1**
1.1 Context . . . 1
1.2 Brief historical review . . . 2
1.3 Plan of the thesis . . . 6

2 Theoretical formalism: the extended local equilibrium approach **9**
2.1 Continuum balance equations . . . 9
2.1.1 Balance of mass . . . 10
2.1.2 Balance of internal energy . . . 10
2.2 Macroscopic non-equilibrium thermodynamics . . . 11
2.2.1 First law . . . 12
2.2.2 Second law . . . 13
2.3 Fluctuating kinetics . . . 15
2.3.1 Fluctuating hydrodynamics . . . 15
2.3.2 Chemical Langevin equations . . . 18
2.4 eLEH stochastic thermodynamics . . . 18
2.4.1 Internal energy balance and first law . . . 19
2.4.2 Stochastic entropy and second law . . . 19

I Stochastic thermodynamics of transport phenomena **21**

3 Stochastic thermodynamics of simple transport processes **23**
3.1 Heat transport . . . 24
3.1.1 Discretisation procedure . . . 24
3.2 Stochastic thermodynamics of heat transport . . . 30
3.2.1 Non-equilibrium steady states . . . 31
Fluctuations of entropy production in a NESS . . . 31
Fluctuations of entropy flux in a NESS . . . 33
3.2.2 Equilibrium states . . . 34
Fluctuations of entropy production at equilibrium . . . 34
Fluctuations of entropy flux at equilibrium . . . 39
3.3 Mass transport . . . 41
3.4 Stochastic thermodynamics of mass transport . . . 44
3.4.1 Non-equilibrium steady states . . . 44
Fluctuations of entropy production in a NESS . . . 45
Fluctuations of entropy flux in a NESS . . . 46

3.4.2 Equilibrium states . . . 46
Fluctuations of entropy production at equilibrium . . . 46
Fluctuations of entropy flux at equilibrium . . . 48
3.5 Stochastic potentials . . . 49
3.5.1 Stochastic Helmholtz free energy and thermodynamic potentials . . . 50
3.5.2 Helmholtz free energy in non-equilibrium steady states . . . 53
3.5.3 Excess entropy production . . . 54
3.5.4 Conclusions about a stochastic potential . . . 58

4 Stochastic thermodynamics of coupled transport processes 61
4.1 Introduction . . . 61
4.2 Deterministic model . . . 62
4.3 Stochastic model . . . 67
4.4 Efficiencies . . . 70
4.4.1 Stochastic separation efficiency . . . 71
Probability distribution of χ_k . . . 71
Fluctuations and efficiency . . . 72
Emergence of the thermodynamic limit . . . 77
4.4.2 Stochastic thermodynamic efficiency . . . 78
Stochastic entropy production . . . 79
Probability distribution of the thermodynamic efficiency . . . 80
Size and sampling time effects on the distribution of thermodynamic efficiency 83
4.5 Conclusions . . . 86

II Stochastic thermodynamics of chemical reactions 89

5 Stochastic thermodynamics of chemical reactions 91
5.1 Introduction . . . 91
5.2 Mesoscopic chemical kinetics . . . 92
5.2.1 Master equations . . . 92
5.2.2 Chemical Langevin equations . . . 94
5.3 Linear chemical reactions . . . 98
5.3.1 Fluctuations of entropy production . . . 100
Fluctuations around equilibrium . . . 102
5.4 Schlögl Model . . . 105
5.4.1 Average dissipation of fluctuations in a non-linear system . . . 106
5.4.2 Fluctuations of entropy production at critical point . . . 109
Fluctuation theorems . . . 110
5.4.3 Beyond the critical point . . . 112
CLE vs. CME modelling . . . 112
Distributions of entropy production . . . 115

Selection principle 118

6 Conclusions and outlook **121**
6.1 Comparison with other stochastic thermodynamic approaches 124
6.2 Perspectives 128

Appendix **131**

A Numerical integration of stochastic differential equations **131**
A.1 Introduction 131
A.2 General theory 131
A.3 Numerical integration 133
A.3.1 Examples 134
A.3.2 Heat transport 134
A.3.3 Schlögl model 135

Bibliography **137**