## Contents

List of Symbols IX Acknowledgments XIII

- 1 Introduction 1 References 14
- 2 Introduction to Time-Reversible, Thermostatted Dynamical Systems, and Statistical Mechanical Ensembles 17
- 2.1 Time Reversibility in Dynamical Systems 17
- 2.2 Introduction to Time-Reversible, Thermostatted Dynamical Systems *19*
- 2.3 Example: Homogeneously Thermostatted SLLOD Equations for Planar Couette Flow *30*
- 2.4 Phase Continuity Equation 32
- 2.5 Lyapunov Instability and Statistical Mechanics 35
- 2.6 Gibbs Entropy in Deterministic Nonequilibrium Macrostates 42
- 2.A Appendix: Phase Space Expansion Calculation 44 References 46
- 3 The Evans–Searles Fluctuation Theorem 49
- 3.1 The Transient Fluctuation Theorem 49
- 3.2 Second Law Inequality 53
- 3.3 Nonequilibrium Partition Identity 55
- 3.4 Integrated Fluctuation Theorem 56
- 3.5 Functional Transient Fluctuation Theorem 58
- 3.6 The Covariant Dissipation Function 59
- 3.7 The Definition of Equilibrium 60
- 3.8 Conclusion 62
  - References 63



٧

## VI Contents

4	The Dissipation Theorem 65
4.1	Derivation of the Dissipation Theorem 65
4.2	Equilibrium Distributions are Preserved by Their Associated Dynamics 68
4.3	Broad Characterization of Nonequilibrium Systems: Driven,
1.5	Equilibrating, and T-Mixing Systems 70
4.3.1	Two Corollaries of the Dissipation Theorem 74
1.0.1	References 75
5	Equilibrium Relaxation Theorems 77
5.1	Introduction 77
5.2	Relaxation toward Mixing Equilibrium: The Umbrella Sampling
	Approach 78
5.3	Relaxation of Autonomous Hamiltonian Systems under
	T-Mixing 83
5.4	Thermal Relaxation to Equilibrium: The Canonical Ensemble 87
5.5	Relaxation to Quasi-Equilibrium for Nonergodic Systems 94
5.6	Aside: The Thermodynamic Connection 94
5.7	Introduction to Classical Thermodynamics 98
5.A	Appendix: Entropy Change for a Cyclic Temperature Variation 104
	References 107
6	Nonequilibrium Steady States 109
6.1	The Physically Ergodic Nonequilibrium Steady State 109
6.2	Dissipation in Nonequilibrium Steady States (NESSs) 111
6.3	For T-Mixing Systems, Nonequilibrium Steady-State Averages are
	Independent of the Initial Equilibrium Distribution 118
6.4	In the Linear Response Steady State, the Dissipation is Minimal with
	Respect to Variations of the Initial Distribution 120
6.5	Sum Rules for Dissipation in Steady States 121
6.6	Positivity of Nonlinear Transport Coefficients 122
6.7	Linear Constitutive Relations for T-Mixing Canonical
	Systems 124
6.8	Gaussian Statistics for T-Mixing NESS 124
6.9	The Nonequilibrium Steady-State Fluctuation Relation 125
6.10	Gallavotti–Cohen Steady-State Fluctuation Relation 129
6.11	Summary 130
	References 131
7	Applications of the Fluctuation, Dissipation, and Relaxation
	Theorems 133
7.1	Introduction 133
7.2	Proof of the Zeroth "Law" of Thermodynamics 134
7.3	Steady-State Heat Flow 137
7.4	Dissipation Theorem for a Temperature Quench 144

## Contents VII

- 7.5 Color Relaxation in Color Blind Hamiltonian Systems 147
- 7.6 Instantaneous Fluctuation Relations 149
- 7.7 Further Properties of the Dissipation Function *151* References *153*
- 8 Nonequilibrium Work Relations, the Clausius Inequality, and Equilibrium Thermodynamics 155
- 8.1 Generalized Crooks Fluctuation Theorem (GCFT) 157
- 8.2 Generalized Jarzynski Equality (GJE) 161
- 8.3 Minimum Average Generalized Work 164
- 8.4 Nonequilibrium Work Relations for Cyclic Thermal Processes 167
- 8.5 Clausius' Inequality, the Thermodynamic Temperature, and Classical Thermodynamics *171*
- 8.6 Purely Dissipative Generalized Work 176
- 8.7 Application of the Crooks Fluctuation Theorem (CFT), and the Jarzynski Equality (JE) *179*
- 8.8 Entropy Revisited 182
- 8.9 For Thermostatted Field-Free Systems, the Nonequilibrium Helmholtz Free Energy is a Constant of the Motion 183 References 184
- **9 Causality** *187*
- 9.1 Introduction 187
- 9.2 Causal and Anti-causal Constitutive Relations 189
- 9.3 Green Kubo Relations for the Causal and Anti-causal Response Functions 190
- 9.4 Example: The Maxwell Model of Viscosity 193
- 9.5 Phase Space Trajectories for Ergostatted Shear Flow 194
- 9.6 Simulation Results 197
- 9.7 Summary and Conclusion 200 References 202

Index 203