

Contents

List of Symbols *IX*

Acknowledgments *XIII*

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

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, Equilibrating, and T-Mixing Systems	70
4.3.1	Two Corollaries of the Dissipation Theorem	74
	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

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

