Contents

Preface XIII
List of Contributors XVII
Color Plates XXIII

Part I Fluctuation Relations 1

1 Fluctuation Relations: A Pedagogical Overview 3
Richard Spinney and Ian Ford
1.1 Preliminaries 3
1.2 Entropy and the Second Law 5
1.3 Stochastic Dynamics 8
1.3.1 Master Equations 8
1.3.2 Kramers–Moyal and Fokker–Planck Equations 9
1.3.3 Ornstein–Uhlenbeck Process 11
1.4 Entropy Generation and Stochastic Irreversibility 13
1.4.1 Reversibility of a Stochastic Trajectory 13
1.5 Entropy Production in the Overdamped Limit 21
1.6 Entropy, Stationarity, and Detailed Balance 25
1.7 A General Fluctuation Theorem 27
1.7.1 Work Relations 30
1.7.1.1 The Crooks Work Relation and Jarzynski Equality 31
1.7.2 Fluctuation Relations for Mechanical Work 34
1.7.3 Fluctuation Theorems for Entropy Production 36
1.8 Further Results 37
1.8.1 Asymptotic Fluctuation Theorems 37
1.8.2 Generalizations and Consideration of Alternative Dynamics 39
1.9 Fluctuation Relations for Reversible Deterministic Systems 41
1.10 Examples of the Fluctuation Relations in Action 45
1.10.1 Harmonic Oscillator Subject to a Step Change in Spring Constant 45
1.10.2 Smoothly Squeezed Harmonic Oscillator 49
1.10.3 A Simple Nonequilibrium Steady State 52
1.11 Final Remarks 54
References 55
2 Fluctuation Relations and the Foundations of Statistical Thermodynamics: A Deterministic Approach and Numerical Demonstration 57
James C. Reid, Stephen R. Williams, Debra J. Searles, Lamberto Rondoni, and Denis J. Evans

2.1 Introduction 57
2.2 The Relations 58
2.3 Proof of Boltzmann’s Postulate of Equal A Priori Probabilities 62
2.4 Nonequilibrium Free Energy Relations 67
2.5 Simulations and Results 69
2.6 Results Demonstrating the Fluctuation Relations 74
2.7 Conclusion 80
References 81

3 Fluctuation Relations in Small Systems: Exact Results from the Deterministic Approach 83
Lamberto Rondoni and O.G. Jepps

3.1 Motivation 84
3.1.1 Why Fluctuations? 85
3.1.2 Nonequilibrium Molecular Dynamics 86
3.1.3 The Dissipation Function 89
3.1.4 Fluctuation Relations: The Need for Clarification 92
3.2 Formal Development 94
3.2.1 Transient Relations 94
3.2.2 Work Relations: Jarzynski 96
3.2.3 Asymptotic Results 98
3.2.4 Extending toward the Steady State 101
3.2.5 The Gallavotti–Cohen Approach 105
3.3 Discussion 108
3.4 Conclusions 110
References 111

4 Measuring Out-of-Equilibrium Fluctuations 115
L. Bellon, J. R. Gomez-Solano, A. Petrosyan, and Sergio Ciliberto

4.1 Introduction 115
4.2 Work and Heat Fluctuations in the Harmonic Oscillator 116
4.2.1 The Experimental Setup 116
4.2.2 The Equation of Motion 117
4.2.2.1 Equilibrium 117
4.2.3 Nonequilibrium Steady State: Sinusoidal Forcing 118
4.2.4 Energy Balance 119
4.2.5 Heat Fluctuations 120
4.3 Fluctuation Theorem 121
4.3.1 FTs for Gaussian Variables 122
4.3.2 FTs for $W_t$ and $Q_t$, Measured in the Harmonic Oscillator 123
4.3.3 Comparison with Theory 125
4.3.4 Trajectory-Dependent Entropy 125
4.4 The Nonlinear Case: Stochastic Resonance 128
4.5 Random Driving 132
4.5.1 Colloidal Particle in an Optical Trap 132
4.5.2 AFM Cantilever 136
4.5.3 Fluctuation Relations Far from Equilibrium 139
4.5.4 Conclusions on Randomly Driven Systems 142
4.6 Applications of Fluctuation Theorems 142
4.6.1 Fluctuation–Dissipation Relations for NESS 143
4.6.1.1 Hatano–Sasa Relation and Fluctuation–Dissipation Around NESS 144
4.6.1.2 Brownian Particle in a Toroidal Optical Trap 144
4.6.2 Generalized Fluctuation–Dissipation Relation 146
4.6.2.1 Statistical Error 146
4.6.2.2 Effect of the Initial Sampled Condition 147
4.6.2.3 Experimental Test 149
4.6.3 Discussion on FDT 149
4.7 Summary and Concluding Remarks 150
References 151

5 Recent Progress in Fluctuation Theorems and Free Energy Recovery 155
Anna Alemany, Marco Ribezzi-Crivellari, and Felix Ritort
5.1 Introduction 155
5.2 Free Energy Measurement Prior to Fluctuation Theorems 156
5.2.1 Experimental Methods for FE Measurements 156
5.2.2 Computational FE Estimates 158
5.3 Single-Molecule Experiments 159
5.3.1 Experimental Techniques 160
5.3.2 Pulling DNA Hairpins with Optical Tweezers 162
5.4 Fluctuation Relations 163
5.4.1 Experimental Validation of the Crooks Equality 165
5.5 Control Parameters, Configurational Variables, and the Definition of Work 166
5.5.1 About the Right Definition of Work: Accumulated versus Transferred Work 168
5.6 Extended Fluctuation Relations 172
5.6.1 Experimental Measurement of the Potential of Mean Force 174
5.7 Free Energy Recovery from Unidirectional Work Measurements 175
5.8 Conclusions 177
References 177
### Part II: Beyond Fluctuation Relations

#### 9 Out-of-Equilibrium Generalized Fluctuation–Dissipation Relations

_G. Gradenigo, A. Puglisi, A. Sarracino, D. Villamaina, and A. Vulpiani_

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.1</td>
<td>285</td>
</tr>
<tr>
<td>9.1.1</td>
<td>286</td>
</tr>
<tr>
<td>9.2</td>
<td>287</td>
</tr>
<tr>
<td>9.2.1</td>
<td>288</td>
</tr>
<tr>
<td>9.2.2</td>
<td>290</td>
</tr>
<tr>
<td>9.2.3</td>
<td>292</td>
</tr>
<tr>
<td>9.2.4</td>
<td>294</td>
</tr>
<tr>
<td>9.3</td>
<td>294</td>
</tr>
<tr>
<td>9.3.1</td>
<td>295</td>
</tr>
<tr>
<td>9.3.2</td>
<td>296</td>
</tr>
<tr>
<td>9.3.3</td>
<td>297</td>
</tr>
<tr>
<td>9.3.4</td>
<td>300</td>
</tr>
<tr>
<td>9.4</td>
<td>301</td>
</tr>
<tr>
<td>9.5</td>
<td>302</td>
</tr>
<tr>
<td>9.5.1</td>
<td>303</td>
</tr>
<tr>
<td>9.5.2</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>9.5.3</td>
<td>Entropy Production</td>
</tr>
<tr>
<td>9.6</td>
<td>Granular Intruder</td>
</tr>
<tr>
<td>9.6.1</td>
<td>Model</td>
</tr>
<tr>
<td>9.6.2</td>
<td>Dense Case: Double Langevin with Two Temperatures</td>
</tr>
<tr>
<td>9.6.3</td>
<td>Generalized FDR and Entropy Production</td>
</tr>
<tr>
<td>9.7</td>
<td>Conclusions and Perspectives</td>
</tr>
<tr>
<td>References</td>
<td></td>
</tr>
</tbody>
</table>

**10**

**Anomalous Thermal Transport in Nanostructures**

*Gang Zhang, Sha Liu, and Baowen Li*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.1</td>
<td>Introduction</td>
<td>319</td>
</tr>
<tr>
<td>10.2</td>
<td>Numerical Study on Thermal Conductivity and Heat Energy Diffusion in One-Dimensional Systems</td>
<td>320</td>
</tr>
<tr>
<td>10.3</td>
<td>Breakdown of Fourier’s Law: Experimental Evidence</td>
<td>325</td>
</tr>
<tr>
<td>10.4</td>
<td>Theoretical Models</td>
<td>327</td>
</tr>
<tr>
<td>10.5</td>
<td>Conclusions</td>
<td>331</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>332</td>
</tr>
</tbody>
</table>

**11**

**Large Deviation Approach to Nonequilibrium Systems**

*Hugo Touchette and Rosemary J. Harris*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.1</td>
<td>Introduction</td>
<td>335</td>
</tr>
<tr>
<td>11.2</td>
<td>From Equilibrium to Nonequilibrium Systems</td>
<td>336</td>
</tr>
<tr>
<td>11.2.1</td>
<td>Equilibrium Systems</td>
<td>336</td>
</tr>
<tr>
<td>11.2.2</td>
<td>Nonequilibrium Systems</td>
<td>339</td>
</tr>
<tr>
<td>11.2.3</td>
<td>Equilibrium Versus Nonequilibrium Systems</td>
<td>340</td>
</tr>
<tr>
<td>11.3</td>
<td>Elements of Large Deviation Theory</td>
<td>341</td>
</tr>
<tr>
<td>11.3.1</td>
<td>General Results</td>
<td>341</td>
</tr>
<tr>
<td>11.3.2</td>
<td>Equilibrium Large Deviations</td>
<td>343</td>
</tr>
<tr>
<td>11.3.3</td>
<td>Nonequilibrium Large Deviations</td>
<td>345</td>
</tr>
<tr>
<td>11.4</td>
<td>Applications to Nonequilibrium Systems</td>
<td>347</td>
</tr>
<tr>
<td>11.4.1</td>
<td>Random Walkers in Discrete and Continuous Time</td>
<td>347</td>
</tr>
<tr>
<td>11.4.2</td>
<td>Large Deviation Principle for Density Profiles</td>
<td>349</td>
</tr>
<tr>
<td>11.4.3</td>
<td>Large Deviation Principle for Current Fluctuations</td>
<td>350</td>
</tr>
<tr>
<td>11.4.4</td>
<td>Interacting Particle Systems: Features and Subtleties</td>
<td>352</td>
</tr>
<tr>
<td>11.4.5</td>
<td>Macroscopic Fluctuation Theory</td>
<td>354</td>
</tr>
<tr>
<td>11.5</td>
<td>Final Remarks</td>
<td>356</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>357</td>
</tr>
</tbody>
</table>

**12**

**Lyapunov Modes in Extended Systems**

*Hong-Liu Yang and Günter Radons*

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.1</td>
<td>Introduction</td>
<td>361</td>
</tr>
<tr>
<td>12.2</td>
<td>Numerical Algorithms and LV Correlations</td>
<td>363</td>
</tr>
<tr>
<td>12.3</td>
<td>Universality Classes of Hydrodynamic Lyapunov Modes</td>
<td>365</td>
</tr>
<tr>
<td>12.4</td>
<td>Hyperbolicity and the Significance of Lyapunov Modes</td>
<td>369</td>
</tr>
</tbody>
</table>
12.5 Lyapunov Spectral Gap and Branch Splitting of Lyapunov Modes in a “Diatomic” System 372
12.6 Comparison of Covariant and Orthogonal HLMs 376
12.7 Hyperbolicity and Effective Degrees of Freedom of Partial Differential Equations 380
12.8 Probing the Local Geometric Structure of Inertial Manifolds via a Projection Method 384
12.9 Summary 388
References 389

13 Study of Single-Molecule Dynamics in Mesoporous Systems, Glasses, and Living Cells 393
Stephan Mackowiak and Christoph Bräuchle
13.1 Introduction 393
13.1.1 Experimental Method 393
13.1.2 Analysis of the Single-Molecule Trajectories 395
13.2 Investigation of the Structure of Mesoporous Silica Employing Single-Molecule Microscopy 396
13.2.1 Mesoporous Silica 396
13.2.2 Combining TEM and SMM for Structure Determination of Mesoporous Silica 398
13.2.3 Applications of SMM to Improve the Synthesis of Mesoporous Systems 399
13.3 Investigation of the Diffusion of Guest Molecules in Mesoporous Systems 402
13.3.1 A More Detailed Look into the Diffusional Dynamics of Guest Molecules in Nanopores 402
13.3.2 Modification of the Flow Medium in the Nanopores and Its Influence on Probe Diffusion 404
13.3.3 Loading of Cargoes into Mesopores: A Step toward Drug Delivery Applications 406
13.4 A Test of the Ergodic Theorem by Employing Single-Molecule Microscopy 407
13.5 Single-Particle Tracking in Biological Systems 409
13.6 Conclusion and Outlook 412
References 413

Index 415