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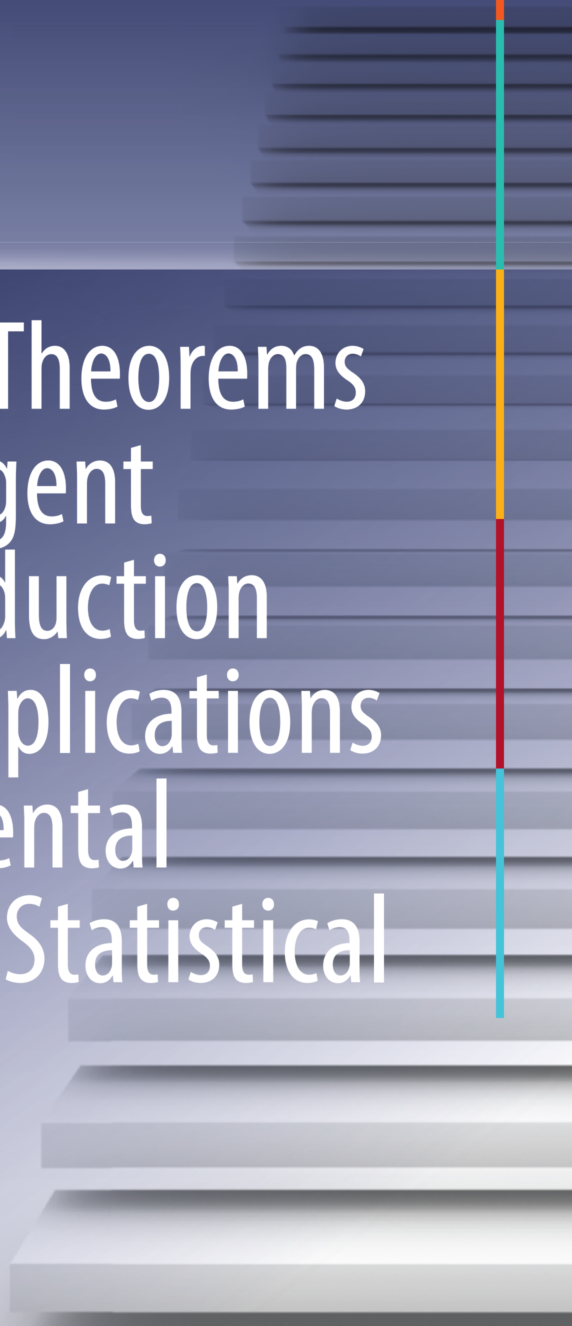

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Yûto Murashita

Fluctuation Theorems under Divergent Entropy Production and their Applications for Fundamental Problems in Statistical Physics

Doctoral Thesis accepted by
University of Tokyo, Tokyo, Japan

Springer

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ISSN 2190-5053 ISSN 2190-5061 (electronic)
Springer Theses
ISBN 978-981-16-8637-5 ISBN 978-981-16-8638-2 (eBook)
https://doi.org/10.1007/978-981-16-8638-2

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Supervisor's Foreword

Understanding macroscopic thermodynamic phenomena from microscopic dynamics is a grand challenge that has hovered over physicists ever since the era of Gibbs and Boltzmann. Over the past quarter century, the fluctuation theorem has played a pivotal role in unveiling several fundamental aspects of emergent irreversibility in systems far from equilibrium. In his thesis, Yuto Murashita studies the fluctuation theorem in extreme yet practically important situations with divergent entropy production and discusses its implications to a few fundamental issues in statistical mechanics.

In the standard framework of the fluctuation theorem, the entropy production is expressed in terms of the ratio of the probability of the original dynamics to that of the time-reversed one. Measure theory tells us that this ratio is not always well defined, especially when entropy production diverges and such cases belong to a new class of irreversibility, which is referred to as absolute irreversibility. Yuto extends the fluctuation theorem so as to be applicable to situations with absolute irreversibility. As a different situation with divergent entropy production, Yuto considers a system which is coupled simultaneously to multiple heat baths at different temperatures as in the case of the Feynman ratchet. In the overdamped limit, the entropy production is divergent since velocities relax not to an equilibrium state but to a nonequilibrium steady state. Despite this singular behavior of the fast degrees of freedom, the fluctuation theorem can be shown for the dynamics of slow degrees of freedom. Furthermore, Yuto applies the fluctuation theorem with absolute irreversibility to two fundamental problems in statistical physics: the Gibbs paradox and the Loschmidt paradox. The Gibbs paradox originates from the problem of gas mixing and is closely connected with the issue in statistical-mechanical problem concerning how to define entropy. Yuto shows that the fluctuation theorem with absolute irreversibility can be utilized as a definition of entropy by considering the gas-mixing process. Finally, Yuto revisits the Loschmidt paradox from the viewpoint of the fluctuation theorem with absolute irreversibility. The Loschmidt paradox concerns how irreversible behaviors emerge from reversible equations of motion. In a closed Hamiltonian system, an imperfect Loschmidt demon is invoked to define an entropy production consistent with the fluctuation theorem. Remarkably, the entropy thus defined exhibits system-specific behavior reminiscent of the Kolmogorov-Sinai entropy and features emergent irreversibility.

I believe that this thesis makes a seminal contribution toward resolving two long-standing problems in statistical physics, namely the Gibbs paradox and the Loschmidt paradox.

Tokyo, Japan
December 2021

Masahito Ueda

Parts of this thesis have been published in the following journal articles:

Y. Murashita, K. Funo and M. Ueda, “Nonequilibrium equalities in absolutely irreversible processes” Physical Review E 90, 042110 (2014). DOI: https://doi.org/10.1103/PhysRevE.90.042110. Parts of Chap. 3 of the thesis are reprinted with permission from this paper. Copyright 2014 by the American Physical Society.

Y. Murashita and M. Esposito, “Overdamped stochastic thermodynamics with multiple reservoirs” Physical Review E 94, 062148 (2016). DOI: https://doi.org/10.1103/PhysRevE.94.062148.

Y. Murashita and M. Ueda, “Gibbs Paradox Revisited from the Fluctuation Theorem with Absolute Irreversibility” Physical Review Letters 118, 060601 (2017). DOI: https://doi.org/10.1103/PhysRevLett.118.060601. Parts of Chap. 5 of the thesis are reprinted with permission from this paper. Copyright 2017 by the American Physical Society.

Y. Murashita, N. Kura and M. Ueda, “Entropy production of a closed Hamiltonian system via the detailed fluctuation relation” Physical Review Research 3, 033224 (2021). DOI: https://doi.org/10.1103/PhysRevResearch.3.033224. Parts of Chap. 6 of the thesis are reprinted from this paper under the Creative Commons Attribution 4.0 International license.

Acknowledgements

The studies in this thesis were conducted when the author was a doctoral student at Prof. Masahito Ueda's group in the University of Tokyo. I would like to express my deep sense of gratitude to my collaborators and colleagues.

First of all, I would like to express my best gratitude to my supervisor, Prof. Masahito Ueda. His inspiring comments and considerable encouragement during our frequent discussions greatly helped me to advance my research. In particular, his critical and constructive comments were indispensable to complete the studies in Chap. 5 and Chap. 6. Furthermore, he read the manuscript of the thesis with great care and gave me enormous suggestions to improve it.

I would like to thank my collaborator, Prof. Massimiliano Esposito. He accepted me as a visiting student at the University of Luxembourg through the oversea dispatch program of my graduate school. Without his extensive expertise or kind support in Luxembourg, the study in Chap. 4 would not be completed.

I am grateful for support from my subadvisor, Prof. Yasunobu Nakamura. He gave me regular opportunities to discuss experimental aspects of our work and taught me on the latest relevant experiments.

I sincerely appreciate considerable assistance from my collaborators. Dr. Naoto Kura regularly discussed with me the study in Chap. 6 and made significant contributions to its mathematical aspects. Dr. Yuta Masuyama frequently visited us to have discussions and taught me fundamentals of experiments of superconducting qubits. Dr. Ken Funo taught me quantum aspects of the fluctuation theorems and gave me enormous opportunities to discuss with. Dr. Tomohiro Shitara helped me to establish mathematical and information-theoretic aspects of our studies. Dr. Yuto Ashida gave me constructive comments from his wide viewpoint to improve impacts and accessibility of our studies. Dr. Zongping Gong taught me key references relevant to our studies on the basis of his comprehensive knowledge of the field.

I would like to express my gratitude to the former and present members of Prof. Ueda's group, especially to Prof. Shunsuke Furukawa and Mrs. Asako Takeuchi, who gave me generous support for my life in the university.

I am also indebted to the members in the University of Luxembourg, especially to Dr. Riccardo Rao, Dr. Artur Wachtel and Dr. Marko Mravlak. They helped me to live a fruitful life there.

I am grateful to Prof. Hosho Katsura and the members of his group for providing me with the office space.

Finally, I acknowledge support from the Japan Society for the Promotion of Science through a fellowship (Grant No. JP15J00410) and the Program for Leading Graduate School (MERIT).

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Chapter 1
Introduction

1.1 Historical Introduction

Equilibrium statistical physics was established by Boltzmann [1] and Gibbs [2, 3] in the late 19th century. It has now wide applications in physics, chemistry, biology and economics and is indispensable for various fields of modern science. In the mid-20th century, linear-response theory [4–7] was developed to describe systems slightly out of equilibrium. Yet, theory applicable to systems far away from equilibrium had been elusive over the following decades.

In 1993, the fluctuation theorem was conjectured in the context of the invariant measure of a chaotic dissipative system and demonstrated by molecular dynamical simulations of a shear-driven fluid in a steady state [8]. The fluctuation theorem states that the probability of entropy decrease is exponentially suppressed compared to that of entropy increase. Remarkably, the fluctuation theorems can be applied to strong driving beyond the linear-response regime. Moreover, they can be regarded as a generalization of linear-response theory in the limit of infinitesimal driving [9]. Although the fluctuation theorems were initially shown in dissipative deterministic systems [10, 11], they were later shown in various systems including stochastic systems such as the Langevin systems [12] and the Markov systems [13]. Thus, the fluctuation theorems are general equalities valid under various kinds of nonequilibrium dynamics and encompass linear-response theory.

However, the fluctuation theorems in their early stage were restricted to systems under time-independent driving. The Jarzynski equality [14] and the Crooks fluctuation theorem [15, 16] were revolutionary in that they apply to systems under time-dependent driving. Later on, fluctuation theorems for various types of entropy productions were derived [17, 18]. The fluctuation theorems have a general structure that the ratio of the probability of the physical process to that of the reference process gives the exponential of the corresponding entropy production [19, 20]. From this perspective, the fluctuation theorems can be understood in a unified way. Thus, the fluctuation theorems give a unified description of nonequilibrium systems under an arbitrary driving.

Y. Murashita, *Fluctuation Theorems under Divergent Entropy Production and their Applications for Fundamental Problems in Statistical Physics*, Springer Theses, https://doi.org/10.1007/978-981-16-8638-2_1

It is noteworthy that the theoretical development of the fluctuation theorems has occurred in excellent synergy with experiments in small thermodynamic systems such as colloidal particles [21] and biomolecules [22]. See Ref. [23] for an extensive review of experimental investigations.

1.2 Present Study

As we have seen in the previous section, the fluctuation theorems are nonequilibrium equalities with a wide applicability, and therefore expected to constitute the foundation of statistical physics. In this thesis, we pose two major questions to the fluctuation theorems. The first question is about their applicability: “How far from equilibrium do they apply?” The second question is about their fundamental significance: “Do they give any novel insight into the foundation of statistical physics?”

Specifically, we consider the fluctuation theorems in two genuinely nonequilibrium situations with divergent entropy production, namely, the situation with absolute irreversibility and the situation with multiple heat reservoirs. Then, we show that the former of them provides us with considerable insights into two fundamental problems in statistical physics, i.e., the Gibbs paradox and the Loschmidt paradox.

The first genuinely nonequilibrium situation is what we call an absolutely irreversible situation. Absolute irreversibility refers to the mathematical singularity of the reference probability measure with respect to the original probability measure, and physically corresponds to negatively divergent entropy production. Due to the singularity, the fluctuation theorems cannot be applied to this situation. Therefore, we should modify the fluctuation theorems into a form that incorporates the degree of absolute irreversibility. This is the study done by the author in his master course.

The second situation is a system simultaneously coupled to multiple heat reservoirs. In this system, when we take the limit of infinitesimal velocity relaxation, the entropy production positively diverges due to the instantaneous transport of heat by the velocities. Consequently, naive overdamped descriptions fail to evaluate thermodynamic quantities. Therefore, we go back to the underdamped description and construct an overdamped approximation by using the technique of the singular expansion. By doing so, overdamped contributions to thermodynamic quantities from the positional degrees of freedom are separated and shown to satisfy the fluctuation theorems.

Then, we apply the fluctuation theorems with absolute irreversibility to the Gibbs paradox [2, 3]. The original discussion of the Gibbs paradox concerns difference between the entropy production upon identical-gas mixing and that upon different-gas mixing [2]. This problem is related to fundamental aspects of thermodynamics and statistical mechanics. Now, the Gibbs paradox collectively refers to issues relating to the dependence of the thermodynamic entropy on the particle number. Among them, we consider the issue to determine the relation between the thermodynamic entropy and the statistical-mechanical entropy. In the thermodynamic limit, it has been known that the requirement of extensivity for the thermodynamic entropy