論文の内容の要旨

Fluctuation theorems under divergent entropy production and their applications for fundamental problems in statistical physics

(発散するエントロピー生成の下での揺らぎの定理とその統計物理学の基礎的問題への応用)

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In the late 19^{th} century, Boltzmann and Gibbs laid the foundation of statistical physics. At that time, the scope of applications was restricted to equilibrium systems. In the mid-20^{th} century, the scope was extended out of equilibrium and linear-response theory was established. Yet, the general theory applicable to systems far from equilibrium had been elusive.

In the 1990's, the fluctuation theorems were discovered. Initially, the theorems were conjectured from an invariant measure of a dissipative chaotic system and numerically demonstrated in molecular dynamical simulations in a shear-driven flow. Then, it was proven on the basis of the chaotic hypothesis for the dissipative chaotic dynamics. The fluctuation theorems apply to systems far from equilibrium and indicate that the probability of a negative entropy production is exponentially suppressed compared with that of the sign-reversed entropy production. Moreover, theory of the fluctuation theorem encompasses linear-response theory in that the fluctuation theorems reproduce the Onsager reciprocity relation and the Green-Kubo relation in the zero limit of driving. Although the first proof of the fluctuation theorems was restricted to dissipative chaotic systems, the fluctuation theorems were later shown under various dynamics such as Hamiltonian dynamics and stochastic dynamics. Today, the fluctuation theorems are nonequilibrium equalities applicable to a wide range of dynamics far from equilibrium.

Although the fluctuation theorems in their early stages concern systems under time-independent driving, they were later extended to systems under time-dependent driving. The most prominent among them are the nonequilibrium work relations including the Jarzynski equality and the Crooks fluctuation theorem. Subsequently the fluctuation theorems were shown to hold for such various thermodynamic quantities as the total entropy production, the excess entropy production and the housekeeping entropy production. Despite this large variety, the fluctuation theorems have a structure in common; the ratio of the probability in the original physical process to that in the reference virtual process, which can be the time-reversed process in some cases, is quantitatively characterized by the exponentiated entropy production. From this unified viewpoint, the fluctuation theorems give a general description of nonequilibrium systems far from equilibrium.

In this thesis, we consider the fluctuation theorems in two extreme situations with divergent entropy production. One is what we call an absolutely irreversible situation, which physically corresponds to negatively divergent entropy production and renders the conventional integral fluctuation theorems inapplicable. In these situations, we should modify the fluctuation theorems to incorporate the degree of absolute irreversibility. The other situation is a system simultaneously coupled to multiple heat reservoirs with different temperatures. In the overdamped limit, the fast degrees of freedom give positively divergent contributions to the entropy production. Nevertheless, we show that the fluctuation theorems hold for contributions from the slow degrees of freedom.

Moreover, we apply the former result, namely, the fluctuation theorems with absolute irreversibility to two fundamental problems in statistical physics: the Gibbs paradox and the Loschmidt paradox. The Gibbs paradox concerns the dependence of the entropy on the particle number and is related to several aspects of foundations of thermodynamics and statistical physics. Among them, we revisit the issue of removing the ambiguity in the relation between the thermodynamic entropy and the statistical-mechanical entropy. Although this issue has already been resolved in the thermodynamic limit by the requirement of extensivity for the thermodynamic entropy, we show that the fluctuation theorem with absolute irreversibility takes the role of extensivity in a small thermodynamic system. Finally, we revisit the Loschmidt paradox in view of the fluctuation theorems with absolute irreversibility. The Loschmidt paradox refers to the argument that macroscopic irreversibility cannot be derived from microscopic reversible dynamics due to the one-to-one correspondence between a path and its time reversal with the sign-inverted entropy production. Nevertheless, as Boltzmann argued, the probability of the paths with positive entropy productions is infinitely more than that of the paths with negative entropy productions. This statement can be verified on the basis of fractality in dissipative systems. Although this fractal scenario seems inapplicable to Hamiltonian systems because of the Liouville theorem, we show that a similar fractality emerges in a chaotic Hamiltonian system in a transient time scale. By expressing this phenomenon in terms of the fluctuation theorems, we bound from below the informational irreversibility by the fractality of a phase-space structure. The linear growth of the bound is reminiscent of the steady entropy production in a steady state of dissipative systems.

The thesis is organized as follows.

In Chap. 1, we introduce a historical background and summarize the contents of this thesis. We also give the outline of the thesis.

In Chap. 2, we introduce fluctuation theorems. First of all, we review the discovery of the fluctuation theorems and see that they are valid for various dynamics and in both steady-state situations and transient situations. Then, we introduce nonequilibrium work relations including the Jarzynski equality and the Crooks fluctuation theorem. Next, we enumerate the fluctuation theorems for various entropy productions, and show that they have the common philosophy that the entropy production quantifies the ratio of the probability in the original process to that in the reference process. Finally, we briefly review the fluctuation theorems under a nonuniform temperature to see that we should be careful to take the overdamped limit in nonisothermal systems.

In Chap. 3, we review the fluctuation theorem in the presence of absolute irreversibility, which is the work in the master thesis of the present author and is therefore not claimed for this thesis. First of all, we see that the fluctuation theorems cannot be applied to free expansion despite their wide applicability. Then, we discuss that this inapplicability physically originates from negatively divergent entropy production and mathematically corresponds to the singularity of the probability measure for the time-reversed paths with respect to that for the original paths. Thus, we mathematically characterize the situations for which the conventional fluctuation theorems are inapplicable, and define them as absolutely irreversible situations. By using the Lebesgue decomposition theorem, we separate the absolutely irreversible contribution and derive the fluctuation theorems that are applicable even in the presence of absolute irreversibility. We confirm their validity in some examples.

In Chap. 4, we consider the overdamped approximation of a system simultaneously coupled to multiple heat reservoirs with different temperatures. In the presence of a single reservoir, the velocity degrees of freedom instantaneously relax to an equilibrium state since the overdamped limit assumes an infinitesimal velocity relaxation time. As a result, the velocity degrees of freedom give no contribution to thermodynamic quantities. However, in the presence of multiple reservoirs, the velocity degrees of freedom relax to a nonequilibrium steady state, which gives a huge contribution to thermodynamic quantities inversely proportional to the velocity relaxation time. Hence, if we naively take the overdamped limit in the presence of multiple reservoirs, we fail to correctly evaluate thermodynamic quantities. Therefore, we start from the underdamped description and construct stochastic thermodynamics for the underdamped dynamics. Then, applying the techniques of the singular expansion to the time-evolution equation of the generating function of thermodynamic quantities, we derive an overdamped description only with the positional degrees of freedom. Remarkably, the fluctuation theorems are shown to hold for thermodynamic contributions from the positional degrees of freedom. Some details of mathematics and derivations are given in Appendix A.

In Chap. 5, we consider the Gibbs paradox in view of the fluctuation theorems with absolute irreversibility. We first review historical discussions of the Gibbs paradox. Then, following van Kampen, we classify it into three related but distinct issues and see that all these issues have already been resolved in the thermodynamic limit. Among them, we revisit the issue concerning the ambiguity of the relation between the thermodynamic entropy and the statistical-mechanical entropy. Although this issue has already been resolved by the requirement of extensivity for the thermodynamic entropy in the thermodynamic limit, this resolution breaks down in a small thermodynamic system. We show that the fluctuation theorem with absolute irreversibility removes the ambiguity in a small thermodynamic system as extensivity does in the thermodynamic limit.

In Chap. 6, we revisit the Loschmidt paradox from the perspective of the fluctuation theorems with absolute irreversibility. We briefly review historical discussions of the Loschmidt paradox. Then, we show that the Loschmidt paradox can be resolved by fractality in phase space in reversible but dissipative systems. Although this fractal scenario of emergent irreversibility seems inapplicable to Hamiltonian systems due to the conservation of the phase-space volume, we demonstrate that a fractal structure emerges in a chaotic Hamiltonian system in a transient time scale. By reformulating this scenario in terms of the fluctuation theorem, we derive the lower bound for the informational irreversibility that is determined by the degree of absolute irreversibility, which has a quantitative relation to the fractal dimension of the phase-space structure in the transient time scale of our interest. Details of mathematics and numerics are given in Appendix B.

In Chap.7, we conclude this thesis. We summarize the results of the thesis and give a brief description of our related work, which is not claimed to be the contents of the thesis. Finally, we describe some future prospects.