The other QFT

Peter Hänggi and Peter Talkner

Fluctuation theorems go beyond the linear response regime to describe systems far from equilibrium. But what happens to these theorems when we enter the quantum realm? The answers, it seems, are now coming thick and fast.

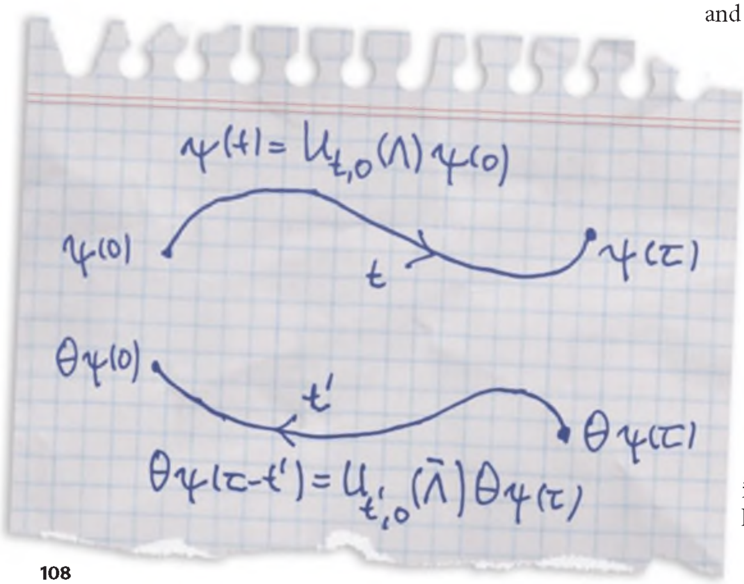
Simply put, fluctuation theorems connect the probabilities for quantities like work, heat or particle number in an experiment to those that would be observed in a time-reversed set-up. Although these relations only hold when both the forward and backward processes start out in thermal equilibrium, they apply to systems that may be subsequently driven arbitrarily far from equilibrium. They are not restricted to the linear response regime, and instead establish exact relations between the non-equilibrium fluctuations of these forward and backward processes, and the equilibrium quantities of the corresponding equilibrium states. Perhaps unsurprisingly, research focused on how this formalism translates to the quantum world has undergone rapid progress in recent years, leading to quantum fluctuation theorems (QFTs), which open up promising new avenues for characterizing the nonlinear transport of energy, charge or heat for quantum devices and engines.

The response of a system to a disturbance can reveal valuable information about the state and properties of the system. Many experimental techniques use this basic effect to determine electrical, magnetic, mechanical, thermal and other properties of materials by means of specifically designed perturbations. Indeed, linear response theory provides a convenient theoretical description of a system's time-dependent reaction to a small perturbation in terms of the fluctuations of the unperturbed system[1–9].

The theory was largely developed in the 1950s for systems initially in thermal equilibrium, and made a name for the likes of Herbert Callen and Theodore Welton[1], as well as Melville Green[2,3] and Ryogo Kubo[4]. These authors extended the notions characterizing systems in thermal equilibrium to describe small deviations from equilibrium. They developed a statistical mechanical basis for Onsager's phenomenological theory[5,6] of non-equilibrium thermodynamics. The linear response of a system far from equilibrium was later related to fluctuations of its unperturbed state — and the concept of a fluctuation theorem was born[9].

Transience and the second law

The transient behaviour of a closed system initially residing in thermal equilibrium subject to an external, time-dependent perturbation for a finite period of time can be understood in terms of the work applied to the system. Looking at the problem in this way led to both the Jarzynski equality[10] and the Crooks relation[11], both of which offer far-reaching understanding about the properties of the statistics of work, w, done by an external perturbation (see refs 12,13 and the Commentary on page 105 for more details).



Work belongs to the most basic notions of physical science. And yet it deserves to be handled with care. For a closed system, the work performed by an external, time-dependent force is determined by the difference between the system energies at the end and the beginning of the force protocol. Work, therefore is not an observable[14].

Briefly, the Jarzynski equality describes the mean value of the exponentiated work applied to a system by the action of a force protocol. The equality is expressed in terms of the difference, ΔF, between the free energies of equilibrium systems corresponding to the initial and final force values and the inverse temperature, β, as $\langle e^{-\beta w}\rangle = e^{-\beta\Delta F}$. Here, ΔF is independent of the details of the force protocol. But the average is performed with respect to the distribution of work, $p_\Lambda(w)$, which does depend on the force protocol (denoted by Λ), and can be related to the analogous distribution for the reverse process (denoted by $\bar{\Lambda}$) through the Crooks relation, $p_\Lambda(w) = e^{-\beta(\Delta F - w)} p_{\bar{\Lambda}}(-w)$.

It follows from the Jarzynski equality that the average work applied to a system by any force must be larger than the change of the free energy, or at least equal to it. This is one way of expressing the second law of thermodynamics — as a consequence of the Jarzynski equality.

The difference between the average work and the change in free energy can be thought of as dissipated work. The idea here is that if, following completion of the force protocol, the system were weakly coupled to a heat reservoir with the temperature of the initial state and the parameter values of the final state, no further work would be needed to equilibrate the system. The dissipated work is thus the amount of energy that would then flow as heat into the reservoir.

Enter quantum mechanics

So far, all of this applies just as well to quantum systems as it does to classical systems. The essential difference arises due to the unavoidable impact that any measurement has on a quantum system. Whereas classical trajectories can be observed — and work determined — without any perturbation to the dynamics, the same approach cannot be applied to a quantum system without seriously influencing its dynamics.

Alternatively, the applied work can be determined by the difference between the outcomes of two energy measurements, one at the beginning and one at the end of the force protocol. Applying this reasoning, one finds that the transient fluctuation relations for quantum mechanics take the same form as the classical relations[14–17]. In other words, the Jarzynski equality and the Crooks relation also apply to quantum systems, provided that the initial and final energies are determined by so-called projective measurements. This means that for a given energy measurement only one eigenvalue of the relevant Hamiltonians is detected, and immediately after the measurement the system remains in the eigenstate corresponding to the measured eigenvalue.

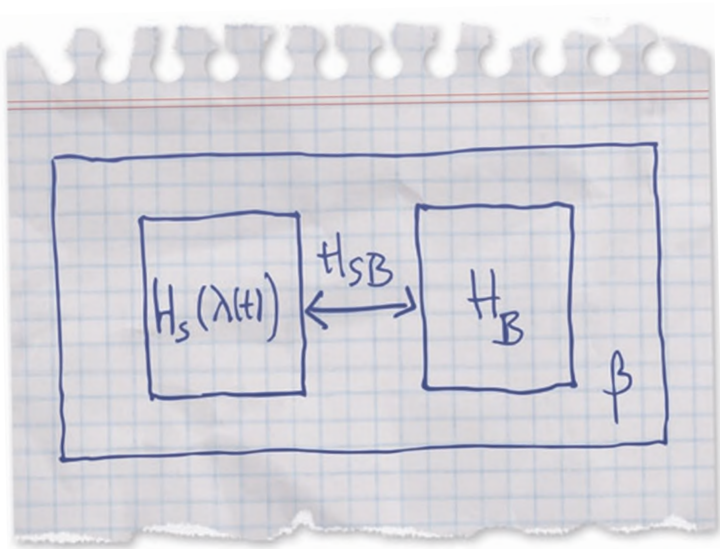
It is well known that this idealized picture of a measurement — which can be traced back to von Neumann[18] — does not always properly describe an actual measurement device and its outcome. However, most other types of measurements are incapable of recovering the transient fluctuation theorems[19,20] because measurements that are not projective typically leave the system in a post-measurement state that differs from the eigenstate corresponding to the measured energy value. These measurements may even come up with an incorrect result for the energy.

It is remarkable, then, that projective measurements of arbitrary observables performed during the force protocol manage to leave the transient fluctuation relations unaffected, even though the work distributions may be substantially altered[21,22]. A large class of generalized intermediate measurements also leaves the fluctuation theorems unchanged[23].

Prerequisites

There are two essential conditions under which transient fluctuation relations hold. The first condition requires canonical equilibrium states for the forward and backward processes. Other initial conditions describing microcanonical or grand canonical states give rise to modified fluctuation relations involving changes of thermodynamic entropy and grand potential, respectively, rather than free-energy changes[24–26].

Time-reversal symmetry (illustrated on the previous page) is the second ingredient. Given a wavefunction, $\psi(t)$, running forward in time according to a protocol-dependent unitary operator $U(\Lambda)$, time-reversal symmetry relates its backward propagation under the action of a time-reversal operator, Θ, to the time-reversed protocol, $\bar{\Lambda}$. Both t and t' start at 0 and run to τ according to the physical arrow of time. This symmetry is fulfilled for a large class of Hamiltonian systems, which most likely covers all physically relevant cases. It relates the inverted dynamics that formally runs backward in time, like a movie in rewind, to a solution of the corresponding time-reversed Hamiltonian system proceeding in physical time[27].



Validation and verification

The Jarzynski equality and the Crooks relation have been experimentally verified for classical systems[28–30] and both have been used as a theoretical basis to determine free-energy differences between different configurations of large molecules in single-molecule experiments[31]. With continuous control of the end-to-end distance of a molecule, for example, together with the known stretching force, the instantaneously applied power and thus the work done on the molecule can be determined. By no means can this technique be readily applied to quantum systems though, because a continuous observation would freeze the dynamics of the quantum system according to the quantum Zeno effect[32]. However, an experimental implementation of the two-energy measurement scheme applied to an ion in a harmonic trap was proposed[33] and recently performed[34], thus validating the Jarzynski equality.

An alternative means of confirming the transient fluctuation relations, which circumvents the experimentally difficult projective-energy measurements, was also recently proposed[35,36]. In this approach, the characteristic function of work — the Fourier transform of the work distribution — is encoded in the reduced density matrix of an auxiliary two-level system. This system interacts with the actual system with a strength whose time dependence is determined by the actual force protocol. A successful experimental verification of the Crooks relation and the Jarzynski equality was reported for a nuclear spin of a carbon atom in a chloroform molecule[37]. A similar approach using an auxiliary quantum system was proposed to test transient fluctuation relations for a light mode in a cavity[38].

Opening up

We have restricted our attention to systems that can gain or lose energy simply by performing work. But this requires that the system under consideration be well isolated from its environment, at least on the timescale of the duration of the force protocol. If not, the environment and its interaction with the system have to be taken into account. In principle, this can always be done in the framework of a Hamiltonian description of the resulting total system.

In this case (pictured left), the total system is initially prepared in a canonical thermal equilibrium state at inverse temperature β. To achieve this initial state, a 'super bath' with the required inverse temperature, β, must weakly couple to the total system. The open system (S), with Hamiltonian $H_S(\lambda(t))$, therefore interacts with its environment (B), with Hamiltonian H_B, through Hamiltonian H_{SB}.

Only parameters, $\lambda(t)$, in the system Hamiltonian, $H_S(\lambda(t))$, can be changed by a force protocol such that work is performed on the system, but not on the surrounding environment. Sooner or later, however, the amount of energy applied to the system will be shared with the environment through their mutual interaction. This means that measurements of the energy of the total system — including the actual system, the environment and interactions between the two — determine the work done on the open system[39].

The transient fluctuation relations hold for the total system provided that it initially stays in a canonical equilibrium state. Again, the work in these relations is performed on the open system. Moreover, the free-energy change of the total system is given by that of the open system, because the free-energy contribution from the environment does not change during the protocol. This is because the force protocol is supposed to act only on the system, not on the environment. In practice, this means that the Jarzynski equality and the Crooks relation are also valid for open systems[39,40], regardless of the nature of the coupling, its strength and the particular nature of the environment.

In the special case of weak coupling, the fraction of energy that contributes to the interaction between the system and the environment can be neglected compared with the energy of the system and the environment. Hence, during a force protocol, a change in the system energy is simply the change in the internal energy of the open system, and a change in the energy of the environment corresponds to the exchanged heat. For the joint probability distribution of the internal energy change, ΔE, and the exchanged heat, Q, a generalized Crooks relation holds, from which the Crooks relation and the Jarzynski equality both follow[41]. However, neither the marginal probability densities of the internal energy nor those of the heat are satisfying these relations.

The generalized Crooks relation for internal energy and heat and an equivalent relation for work and heat are valid independent of the nature of the environment, and therefore also apply to open systems undergoing non-Markovian dynamics. This requires that the total system initially is in thermal equilibrium, and that the open system is weakly coupled to its environment. A consistent definition of heat is currently not known for systems coupled strongly to their environment. In particular, a means of properly assigning an interaction energy to the system and its environment is still missing.

Many reservoirs

Our discussion has focused on cases in which the environment and system initially reside in thermal equilibrium. But much richer scenarios emerge when the environment consists of distinct reservoirs that are not in equilibrium with one another — with different temperatures and/or chemical potentials for one or several particle species. In cases such as these, each reservoir is assumed to be large enough that together they can maintain a steady state in the system for a sufficiently long time. And such a steady state will be able to carry currents of heat, charge and neutral particles.

The so-called exchange fluctuation relations connect the probabilities of currents flowing in the direction of and opposite to the bias imposed by these reservoirs[21,42,43]. Additional time-dependent modifications of the central system coupling the reservoirs to each other also perform work, which can be incorporated into the exchange fluctuation relations[44,45].

The way from here

As exact relations, both the transient and the steady-state exchange fluctuation theorems provide deep insight into the energy and transport properties of processes far from thermal equilibrium. The experimental verification of the transient fluctuation relations, in particular, is still in its infancy — with some promising first results.

Classically, a system can be continuously monitored — with unlimited precision (in principle) and without negative effects on the system. But in quantum mechanics, a continuous observation is enough to freeze the dynamics of the system. Therefore, a quantum analogue of a classical trajectory is not at our disposal and the experimental techniques that are employed to verify the quantum fluctuation relations and use them for determining free-energy changes cannot be directly transferred to the quantum regime.

On the whole, the quantum fluctuation theorems present far fewer problems than the experimental challenges we have yet to face. However, some theoretical problems remain to be addressed, including, for example, a clear definition of heat as a fluctuating quantity in the presence of strong coupling between a system and its reservoir. Another issue is related to the fact that the present derivation of exchange fluctuation theorems is based on an initial product state for the system and the different reservoirs. A more realistic initial state that also incorporates correlations and entanglement of system and reservoirs would be advantageous, and may even resolve some of the present discrepancies between theory and experiment.

Further research in this direction will not only provide a better understanding of non-equilibrium quantum processes, but may also help in engineering nanoscopic machines, pumps and data-processing operations on the quantum level. For these applications, a shift of paradigm from processes driven by prescribed protocols towards controlled quantum processes might be useful.

In any case, the quantum fluctuation theorems inherit their specific beauty as exact results. ❐

Peter Hänggi and Peter Talkner are in the Institute of Physics at the University of Augsburg, 86135 Augsburg, Germany.
e-mail: hanggi@physik.uni-augsburg.de

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