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Work, dissipation, and fluctuations in nonequilibrium physics

Quantum fluctuation theorem: can we go from micro to meso?

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Abstract

Quantum extensions of the Gallavotti–Cohen fluctuation theorem (FT) for the entropy production have been discussed by several authors. There is a practical gap between microscopic forms of FT and mesoscopic (i.e. not purely Hamiltonian) forms for open systems. In a microscopic setup, it is easy to state and to prove FT. In a mesoscopic setup, it is difficult to identify fluctuations of the entropy production. (This difficulty is absent in the classical case.) We discuss a particular mesoscopic model: a Lindblad master equation, in which we state FT and, more importantly, connect it rigorously with the underlying microscopic FT. We also remark that FT is satisfied by the Lesovik–Levitov formula for statistics of charge transport. ***To cite this article: W. De Roeck, C. R. Physique 8 (2007).***
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Résumé

Théorème de fluctuations quantiques : peut-on aller du micro au méso ? Des extensions quantiques du théorème de fluctuations (TF) de Gallavotti et Cohen pour la production d'entropie ont été discutées par plusieurs auteurs. Il y a une séparation pratique entre les formes microscopiques du TF et les formes mésoscopiques (c'est-à-dire non purement hamiltoniennes) pour les systèmes ouverts. Dans un schéma microscopique, il est facile d'énoncer et de démontrer le TF. Dans un schéma mésoscopique, il est difficile d'identifier les fluctuations de la production d'entropie. (Cette difficulté est absente dans le cas classique.) Nous discutons un modèle mésoscopique particulier : une équation maîtresse de Lindblad pour laquelle nous énonçons le TF et, ce qui est plus important, nous le connectons rigoureusement avec le TF microscopique. Nous remarquons aussi que le TF est satisfait par la formule de Lesovik–Levitov pour la statistique du transport de charges. ***Pour citer cet article : W. De Roeck, C. R. Physique 8 (2007).***
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1. Introduction

A goal of nonequilibrium statistical mechanics is to make good, yet simple, models of complicated phenomena out of equilibrium and to analyze them. Such models should answer correctly questions like: "What is the structure of an object's state that is kept between two heat reservoirs at different temperatures? How does it look like locally and how does it fluctuate?" or "When and how does a liquid flow become turbulent?". In equilibrium, we have a good and simple guiding rule for making dynamical models: *detailed balance*. Surely, any nonequilibrium dynamics should break detailed balance, but can one formulate a general rule as to how to fix this detailed balance breaking?

It is here that the celebrated Gallavotti–Cohen fluctuation theorem (FT) (see [1–3]) for the entropy production comes into the picture. It turns out that there is such a general rule and it reads (for every path σ of the dynamics, with corresponding probability $\mathrm{Prob}[\sigma]$)

$$\log \frac{\mathrm{Prob}[\sigma]}{\mathrm{Prob}[\theta\sigma]} = \text{Entropy production along } \sigma + \mathrm{o}(t) \tag{1}$$

where $\theta\sigma$ is the time reversed path σ. The FT itself

$$\log \frac{\mathrm{Prob}[\text{Entropy production up to time } t \text{ equals } st]}{\mathrm{Prob}[\text{Entropy production up to time } t \text{ equals } -st\ ]} = st + \mathrm{o}(t) \tag{2}$$

is an immediate consequence of the above rule (1). The LHS are expected to be linear in time t, the $\mathrm{o}(t)$ term vanishes after dividing by t and taking $t \uparrow \infty$. See [4] for a discussion focusing on the universality of (1).

For our purposes, it is good to emphasize that there are two reasons to appreciate (1), (2), even if those reasons are obviously intimately related:

(I) Formulas (1) and (2) can be derived on a microscopic level, starting with Hamiltonian dynamics, using its time-reversibility and identifying entropy production as the log of phase space volume. This was outlined in [5].
(II) The rules (1) and (2) do apply to a lot of effective (not purely Hamiltonian) or mesoscopic models. It is actually in effective models that the FT was observed and that it is studied most often. In [1–3], one treats thermostatted systems, while in e.g. [6–8], as well as in most later publications, one deals with stochastic models.

Note that (II) does morally, but not exactly follow from (I) since mesoscopic or effective models are *merely* good approximations of the Hamiltonian microscopic dynamics.

This article is concerned with the question how rules (1) and (2) extend to quantum mechanics. On the microscopic level (cf. (I) above), there is an obvious problem with deriving (1); quantum mechanics does not have the concept of paths with associated pathwise entropy production. However, (2) still makes sense and, in fact, it remains true, as was pointed out in [9–12] and as we review in a streamlined version in Section 2.

As to the status of quantum FT in effective or mesoscopic models (cf. (II)), the majority of research has focused on master equations for small systems (see recently [13]). A very explicit discussion can be found in [14], a simplified version of which is presented in Section 3.3. The ideas developed there are also implicit in [12] and [15].

The fact that not more effective or mesoscopic models have been investigated is perhaps not too surprising. With the possible exception of the master equations discussed in Section 3, there are not many Markovian models of open quantum systems which are healthy in all respects. One frequent pathology is the appearance of nonpositive density matrices. A review of this problem and a list of possible approaches is given in [16]. We should mention that these problems are not inherent to nonequilibrium models. Already the notion of detailed balance is somehow problematic for Markovian quantum models since the existing definitions [17,18] are so restrictive that the master equation in Section 3 is *essentially* the sole example.

Moreover, even if one has a trustworthy model, there still remains to identify the fluctuating entropy production. It should be clear from Section 3 and Remark 1 in Section 3.3 that this is not trivial.

We remark hence that in quantum mechanics, there is a practical gap between (I) and (II). This might be disconcerting, but possibly it also offers opportunities: perhaps one can improve upon some models of open quantum systems *by imposing FT*.

In the case of master equations which we treat in this article, not only (2) holds but there is also a convenient framework to state (1). This framework is the formalism of *unraveling of master equations*. Our results imply that these unravelings are rigorously linked to fluctuations of currents. This is discussed extensively in [19].

1.1. Brief summary

In Section 2, we review and sharpen the Hamiltonian approach to the FT. In Section 2.3, we give an example of a known counting formula in mesoscopic physics which satisfies FT. We introduce the master equation describing a small system in contact with different heat baths in Section 3 and we develop the necessary tools (unravelings) to identify the entropy production. Finally, in Section 4, we connect the master equation with the Hamiltonian approach and we show that fluctuations of the entropy production in the Hamiltonian model converge to fluctuations calculated by means of unravelings. The importance of this result is:

(1) It shows that the FT is valid in the thermodynamic limit (at least in the weak coupling limit);
(2) It rigorously justifies the technique of unravelings, which is quite popular in quantum optics.

2. The quantum fluctuation theorem

To fix our thoughts, we introduce a model and corresponding notation. Imagine several heat reservoirs indexed by $k \in K$ and modeled by Hilbert spaces $\mathcal{H}_k$ and self-adjoint Hamiltonians H_k on $\mathcal{H}_k$. Each reservoir is in thermal equilibrium at inverse temperature β_k. One connects all heat reservoirs with a small system S, modeled by a finite-dimensional Hilbert space $\mathcal{H}_\mathrm{S}$ and a self-adjoint Hamiltonian H_S. The connection between S and reservoir k is through a self-adjoint coupling term $H^\mathrm{I}_{\mathrm{S}-k}$ on $\mathcal{H}_\mathrm{S} \otimes \mathcal{H}_k$. The coupling is controlled by a factor λ and the total Hamiltonian is

$$H_\lambda = H_\mathrm{S} + \sum_k H_k + \lambda \sum_k H^\mathrm{I}_{\mathrm{S}-k} \tag{3}$$

The dynamics of the full system is given by the unitary group $U^\lambda_t = \mathrm{e}^{-\mathrm{i}tH_\lambda}$ on the Hilbert space $\mathcal{H} := \mathcal{H}_\mathrm{S} \otimes [\bigotimes_k \mathcal{H}_k]$. The initial state ρ_0 is a product state on $\mathcal{H}$

$$\rho_0 = \mu_0 \otimes \left[\bigotimes_k \rho_{k,\beta_k}\right] \tag{4}$$

where the states ρ_{k,β_k} are equilibrium states on $\mathcal{H}_k$ with respect to the Hamiltonians H_k at inverse temperatures β_k and μ_0 is an arbitrary density matrix on $\mathcal{H}_\mathrm{S}$.

In the thermodynamical limit, the states ρ_{k,β_k} are no longer density matrices and one needs the machinery of operator algebras, see e.g. [20,21], to define these states properly. We will completely ignore this problem (since its solution belongs to standard knowledge in mathematical physics), and we avoid writing ill-defined expressions by using the notation

$$\rho_k[A] := \mathrm{Tr}[\rho_k A] \quad \text{with } A \text{ an operator and } \rho_k \text{ a density matrix on } \mathcal{H}_k \tag{5}$$

The LHS can still be used when ρ_k is no longer a density matrix, but instead a state in the sense of operator algebras.[2] Note finally that models as (3) have received a lot of attention lately in mathematical physics. E.g. in [22] one proves the Green–Kubo relations and Onsager reciprocity in the spin-fermion model at finite $\lambda > 0$.

2.1. What do we mean by quantum fluctuations?

It is not a priori clear what one means by fluctuations of heat currents, or fluctuations of the entropy production. (See [23] for an elaboration on that question.)

One encounters at least three approaches (see, however, [23] for a different view).

(1) Measure the energies H_k in the beginning and at the end of the experiments and make statistics of the difference of both measurements. This approach yields the FT [12,9,10,24].

[2] In fact, the situation is even more complicated. For fermions, one can indeed find a subalgebra of $\mathcal{B}(\mathcal{H}_k)$—the Weyl-$\mathcal{C}^*$-algebra—on which the state ρ_{k,β_k} can be appropriately defined. For bosons, one has to invoke W^*-algebras and the Araki–Woods representation to give rigorous meaning to the model.

(2) Calculate the fluctuations of the operator $U_t H_k U_{-t} - H_k$. In [25], a deviation from the fluctuation theorem was established for the fluctuations of a related operator.
(3) In [26], one studies the fluctuations of the *relative modular operator*—a C^*-algebraic concept. These fluctuations satisfy the FT, but the meaning of this relative modular operator is a priori unclear to us.

The advantage of the first approach is that it is more relevant in an experimental setup. A possible argument for the second would be that it seems better suited for taking the thermodynamic limit, since it avoids the measurements. However, by slightly reformulating the first approach, one can also meaningfully study the thermodynamical limit (see also [27]), as we point out now.

Assume for simplicity that the H_k have discrete spectra, indicating that we have not taken the thermodynamic limit and let $x \in X$ label a complete set of eigenvectors $|x\rangle$ of $(H_k)_{k\in K}$ with eigenvalues $(H_k)_{k\in K}(x)$. Let the projectors P_x stand for $1 \otimes |x\rangle\langle x|$ where 1 stands for identity on $\mathcal{H}_S$. The probability of measuring an entropy production r is

$$\mathbb{P}_{t,\lambda}(r) = \sum_{x,y\in X,\, \sum_k \beta_k (H_k(y)-H_k(x))=r} \rho_0\big[P_x U_{-t}^{\lambda} P_y U_t^{\lambda} P_x\big] \tag{6}$$

The idea behind the formula is clear: measure (thereby projecting on the eigenstates x), then switch on the time evolution U_t^{λ}, finally measure again (projecting on the eigenstates y). For later convenience, instead of studying the probability distribution $\mathbb{P}_{t,\lambda}(r)$, we focus on the Laplace transform.

$$F(\kappa, t, \lambda, \rho_0) := \int_{\mathbb{R}} \mathrm{d}\mathbb{P}_{t,\lambda}(r) \mathrm{e}^{-\kappa r} \tag{7}$$

which, in the case when $\mathbb{P}_{t,\lambda}(r)$ is given by (6), reads

$$F(\kappa, t, \lambda, \rho_0) := \sum_{x,y\in X} \rho_0\big[P_x U_{-t}^{\lambda} P_y U_t^{\lambda} P_x\big] \mathrm{e}^{-\kappa \sum_k \beta_k (H_k(y)-H_k(x))} \tag{8}$$

We now use that the initial state ρ_0 is diagonal in the basis $|x\rangle$ to rewrite (8) into

$$F(\kappa, t, \lambda, \rho_0) = \rho_0\big[U_{-t}^{\lambda} \mathrm{e}^{-\kappa \sum_k \beta_k H_k} U_t^{\lambda} \mathrm{e}^{\kappa \sum_k \beta_k H_k}\big] \tag{9}$$

This last expression is perfectly suited for taking the thermodynamic limit, since it remains well-defined when the operators H_k have continuous spectrum and the state ρ_0 is not given by a density matrix. (This does not mean that the expression (9) is necessarily finite. After all, the physics could be such that the Laplace transform is infinite for some κ.)

2.2. *Derivation of the quantum fluctuation theorem*

If one defines the fluctuations through (9), FT is easily derived. Assume that the initial state ρ_0 is given by

$$\rho_0 = \frac{1}{d} \otimes \left[\bigotimes_k \frac{\mathrm{e}^{-\beta_k H_k}}{Z_k}\right], \quad Z_k := \mathrm{Tr}\, \mathrm{e}^{-\beta_k H_k},\ d := \dim \mathcal{H}_S \tag{10}$$

hence the initial state on the small system is the trace state, or infinite temperature state. Assume further that the dynamics is reversible, i.e. there is an anti-unitary time-reversal involution T which commutes with both the free and interacting Hamiltonians

$$[T, H_k] = 0, \qquad [T, H_\lambda] = 0, \qquad TT = 1, \qquad T U_t^{\lambda} T = U_{-t}^{\lambda} \tag{11}$$

Abbreviating $W = \sum_k \beta_k H_k$, using the above relations and cyclicity of the trace, one calculates

$$F(\kappa, t, \lambda, \rho_0) = \mathrm{Tr}\big[\mathrm{e}^{-W} TTU_t^{\lambda} TT \mathrm{e}^{-\kappa W} TTU_{-t}^{\lambda} TT \mathrm{e}^{\kappa W}\big]\left(d \prod_k Z_k\right)^{-1} \tag{12}$$

$$= \mathrm{Tr}\big[\mathrm{e}^{-W} U_t^{\lambda} \mathrm{e}^{-(1-\kappa)W} U_{-t}^{\lambda} \mathrm{e}^{(1-\kappa)W}\big]\left(d \prod_k Z_k\right)^{-1} = F(1-\kappa, t, \lambda, \rho_0) \tag{13}$$

which is equivalent to (2) without the $o(t)$-correction term. The above derivation relies on a particular initial state for the small system. It is known as a transient FT. Obviously, for large t, one expects the initial state of the small system to be irrelevant and (2) follows under some additional ergodicity assumptions.

2.3. Example: counting statistics for charge transport

As argued in Section 1, it is interesting to investigate to what extent the fluctuation symmetry is actually present in known expressions for current statistics. We briefly discuss the Lesovik–Levitov formula [28] for electronic transport between leads. We base our treatment on a neat version of the formula presented in [27] wherein the electrons do not interact and the formula (16) can be derived without any approximation. It is also assumed that all Hilbert spaces are finite-dimensional (see [29] for a discussion of the thermodynamical limit).

Let $\mathfrak{h}$ be the Hilbert space of one electron. The presence of two leads is made explicit by splitting $\mathfrak{h} = \mathfrak{h}_1 \oplus \mathfrak{h}_2$ where the spaces $\mathfrak{h}_1, \mathfrak{h}_2$ contain all the states in respectively lead 1, 2. The projectors on $\mathfrak{h}_1, \mathfrak{h}_2$ are denoted $1_{\mathfrak{h}_1}, 1_{\mathfrak{h}_2}$ and the decoupled one-particle Hamiltonian is $h_1 \oplus h_2$. Let the inverse temperature be β and let the leads have respective chemical potentials μ_1, μ_2. Let n be the occupation number operator (dictated by Fermi–Dirac statistics)

$$n = \left(\mathrm{e}^{\beta(h_1-\mu_1 1_{\mathfrak{h}_1})}\mathrm{e}^{\beta(h_2-\mu_2 1_{\mathfrak{h}_2})} + 1\right)^{-1} \tag{14}$$

The contact between the leads is modeled by a scattering process with unitary scattering matrix S. We assume, that the scattering process conserves total energy and that both scattering process and decoupled evolution are reversible

$$[S, h_1 \oplus h_2] = 0, \qquad T h_{1,2} T = h_{1,2}, \qquad TST = S^* \tag{15}$$

for some anti-unitary operator T modeling time-reversal.

At time $t = 0$ and $t = \tau$, one measures the total charge in, say, lead 1 (for simplicity, we set the charge to unity, so that 'charge' just means 'number of particles'). Let $F(\kappa)$ be the Laplace transform of the distribution of transported charge $F(\kappa) = \sum_{q=-\infty}^{+\infty} p(q)\mathrm{e}^{-\kappa q}$ where $p(q)$ is the probability to find at time $t = \tau$ an excess charge q, as compared to $t = 0$.

The Lesovik–Levitov formula reads (see [27]):

$$F(\kappa) = \det\left(1 + n\left(S^* \mathrm{e}^{-\kappa 1_{\mathfrak{h}_1}} S \mathrm{e}^{\kappa 1_{\mathfrak{h}_1}} - 1\right)\right) \tag{16}$$

Obviously, the entropy production in this scenario is just $-\beta(\mu_1 - \mu_2)q$ and hence one expects that FT implies the following symmetry (cf. (12), (13))

$$F\left(-\kappa\beta(\mu_1 - \mu_2)\right) = F\left(-(1-\kappa)\beta(\mu_1 - \mu_2)\right) \tag{17}$$

That relation is easily verified by starting from (16), using (15) and the fact that $\det(AB) = \det(A)\det(B)$ for matrices A, B (recall that our one-fermion space is finite-dimensional).

3. A good effective model: the master equation

3.1. Construction of the master equation

Having in mind the Hamiltonian model introduced in Section 2, we can construct a master equation that approximates the evolution of a general density matrix μ_0 on the small system $\mathcal{H}_S$. This master equation describes essentially[3] two effects:

(1) Decoherence: non-diagonal elements in the eigenbasis of H_S vanish;
(2) The fluctuations of the diagonal elements, which evolve independently of the off-diagonal elements.

In view of this behavior, we choose to restrict attention to diagonal elements. This allows for a less technical presentation, as we can replace the Lindblad master equation by a classical Markov process.

[3] That is, if we assume H_S to be nondegenerate. If it is degenerate, the picture is slightly more complicated but the results still hold, see [14].

Let $e, e', \ldots$ be the eigenvalues of the system Hamiltonian H_{S} and let $P_e, P_{e'}, \ldots$ be the projectors on the corresponding eigenspaces which we assume one-dimensional.

Define transition probabilities for each separate $k \in K$ as

$$p_k(e, e') := \int_{\mathbb{R}} \mathrm{d}t \mathrm{e}^{\mathrm{i}t(e'-e)} (1 \otimes \rho_{k,\beta_k}) \big[\mathrm{e}^{\mathrm{i}H_k t} P_{e'} H^{\mathrm{I}}_{\mathrm{S}-k} P_e \mathrm{e}^{-\mathrm{i}H_k t} P_e H^{\mathrm{I}}_{\mathrm{S}-k} P_{e'}\big] \tag{18}$$

where 1 is the (unnormalized) density matrix 1 on $\mathcal{H}_{\mathrm{S}}$. The total transition probabilities are hence given as

$$p(e, e') = \sum_k p_k(e, e') \tag{19}$$

The information about the temperatures β_k is encoded into the RHS of (18) through the state ρ_k and in fact one can show

$$\text{Reservoir } k \text{ is at thermal equilibrium at } \beta_k \Rightarrow p_k(e, e')/p_k(e', e) = \mathrm{e}^{\beta_k(e-e')} \tag{20}$$

As said, the density matrix of the system is diagonal. We denote the time-dependent diagonal elements by $\mu_e(t)$. The (Pauli) master equation now reads

$$\frac{\mathrm{d}\mu_e(t)}{\mathrm{d}t} = \sum_{e'} \big(\mu_{e'}(t) p(e', e) - \mu_e(t) p(e, e')\big) \tag{21}$$

3.2. Derivation of the master equation

The only information missing is in what sense this master equation (21) approximates the true dynamics generated by (3). Physically, one needs to perform the Born–Markov approximation and the rotating wave approximation, on which we will not comment here (see instead [30,31]). Mathematically, one can make the convergence to the master equation precise in the so-called weak coupling limit: let the initial state $\rho_0 = \mu_0 \otimes [\bigotimes_k \rho_{k,\beta_k}]$ be as in (4). Let $\mu^\lambda(t)$ be the density matrix obtained by reducing the full state of the interacting system at time t, i.e.

$$\mu^\lambda(t) = \mathrm{Tr}_{\mathrm{R}} \left[U^\lambda_t \mu_0 \otimes \left[\bigotimes_k \rho_{k,\beta_k} \right] U^\lambda_{-t} \right] \tag{22}$$

where Tr_{R} is a conditional expectation. (If ρ is a state on $\mathcal{H}_{\mathrm{S}} \otimes \mathcal{H}_{\mathrm{R}}$, then $\mathrm{Tr}_{\mathrm{R}}\, \rho$ is a state on $\mathcal{H}_{\mathrm{S}}$ such that for any operator A on $\mathcal{H}_{\mathrm{S}}$: $\rho(A) = (\mathrm{Tr}_{\mathrm{R}}\, \rho)(A)$. If ρ is a density matrix, then Tr_{R} is just the partial trace over the reservoirs.) The statement, rigorously proven in [32] under mild assumptions (about which we will be more explicit in Section 4), is

$$P_e \mu^\lambda\big(\lambda^{-2} t\big) P_e \underset{\lambda \searrow 0}{\longrightarrow} \mu_e(t) \tag{23}$$

As is clear from the scaling and the expression (18), the master equation emerges in second-order perturbation theory. Hence we require that $\mathrm{Tr}_{\mathrm{R}}[H^{\mathrm{I}}_{\mathrm{S}-k}] = 0$ such that the first order term perturbation term vanishes (which can always be achieved by redefining H_{S}).

3.3. Guessing path-wise entropy production

Given the very suggestive form of the transition probabilities (18), one is inclined to supplement the master equation in the following way:

The paths σ of the Markov process defined by formula (21) are sequences of energy levels e_i with transition times t_i (jump from e_{i-1} to e_i) with $\mathbb{P}^t_{e_0}$ the path probabilities up to time t

$$\sigma = (e_0; t_1, e_1; t_2, e_2; \ldots; t_n, e_n), \qquad \mathbb{P}^t_{e_0}(\sigma) = \mathrm{e}^{-\lambda_{e_0} t_1} p(e_0, e_1) \mathrm{e}^{-\lambda_{e_1}(t_2 - t_1)} \cdots p(e_{j-1}, e_j) \mathrm{e}^{-\lambda_{e_j}(t - t_j)} \tag{24}$$

where j is the highest index such that $t_j < t$ and $\lambda_e = \sum_{e'} p(e, e')$ are the escape rates. The subscript e_0 in $\mathbb{P}^t_{e_0}$ indicates the process has been started from e_0.

Clearly, to speak about currents and entropy production, we need more information; we need to know which bath k *triggered* the transition. Hence, we need a process with paths $\tilde{\sigma}$ and probabilities $\tilde{\mathbb{P}}^t_{e_0}(\tilde{\sigma})$:

$$\begin{aligned}\tilde{\sigma} &= (e_0; t_1, k_1, e_1; t_2, k_2, e_2; \ldots; t_n, k_n, e_n)\\ \tilde{\mathbb{P}}^t_{e_0}(\tilde{\sigma}) &= \mathrm{e}^{-\lambda_{e_0} t_1} p_{k_1}(e_0, e_1)\mathrm{e}^{-\lambda_{e_1}(t_2-t_1)} \cdots p_{k_j}(e_{j-1}, e_j)\mathrm{e}^{-\lambda_{e_j}(t-t_j)}\end{aligned} \tag{25}$$

We simply define a new process corresponding to the pathspace measure (25). Remark that obviously,

$$\sum_{\tilde{\sigma}\to\sigma} \tilde{\mathbb{P}}^t_{e_0}(\tilde{\sigma}) = \mathbb{P}^t_{e_0}(\sigma) \tag{26}$$

where the sum is over all $\tilde{\sigma}$ which reduce to σ by omitting all k_i.

One can just as well calculate the matrix elements $\mu_e(t)$ from the path probabilities $\tilde{\mathbb{P}}$ as from $\mathbb{P}$:

$$\mu_e(t) = \sum_{\tilde{\sigma}, e_{n(\tilde{\sigma})}=e} \tilde{\mathbb{P}}^t_{\mu(0)}(\tilde{\sigma}) = \sum_{\sigma, e_{n(\sigma)}=e} \mathbb{P}^t_{\mu(0)}(\sigma) \tag{27}$$

where

$$\tilde{\mathbb{P}}^t_{\mu(0)} = \sum_{e_0} \mu_{e_0}(0)\tilde{\mathbb{P}}^t_{e_0}, \qquad \mathbb{P}^t_{\mu(0)} = \sum_{e_0} \mu_{e_0}(0)\mathbb{P}^t_{e_0} \tag{28}$$

and with $n(\tilde{\sigma}), n(\sigma)$ being the number of jumps in the paths $\tilde{\sigma}, \sigma$. Hence, we have extended our pathspace probability measure $\mathbb{P}^t$ into a pathspace probability measure $\tilde{\mathbb{P}}^t$. In the theory of open quantum systems, one calls such an extension an *unraveling* and the paths $\tilde{\sigma}$ are called *quantum trajectories*, see [31,33] for an overview and [34] for similar reasoning.

Having the pathspace probability measure $\tilde{\mathbb{P}}^t$ at our disposal, we can do all the manipulations which are familiar from classical Markov processes. The function on paths $\tilde{\sigma}$

$$w^t(\tilde{\sigma}) = -\sum_{i=1}^{n} \beta_{k_i}(e_i - e_{i-1}) \tag{29}$$

which we identify as the path dependent entropy production, is equal to the ratio of probabilities of forward and backward paths;

$$w^t(\tilde{\sigma}) = \log \frac{\mathrm{d}\tilde{\mathbb{P}}_{\mu_0}(\tilde{\sigma})}{\mathrm{d}\tilde{\mathbb{P}}_{\mu_t}(\theta\tilde{\sigma})} \quad \text{with } \theta\tilde{\sigma} = (e_n; t-t_n, k_n, e_{n-1}; \ldots; t-t_2, k_2, e_2; t-t_1, k_1, e_0) \tag{30}$$

as follows from (20). From (30), we retrieve the FT (2), or its Laplace-transformed version

$$\log \int \mathrm{d}\tilde{\mathbb{P}}^t_{\mu_0}(\tilde{\sigma})\mathrm{e}^{-\kappa w^t(\tilde{\sigma})} = \log \int \mathrm{d}\tilde{\mathbb{P}}^t_{\mu_0}(\tilde{\sigma})\mathrm{e}^{-(1-\kappa)w^t(\tilde{\sigma})} + \mathrm{o}(t) \tag{31}$$

Obviously, one can push on and prove the Green–Kubo relations, Onsager reciprocity and strict positivity of the entropy production from (31). This is discussed at length in [14].

At this point, one should note that this *unraveling* and the construction of the pathspace measure $\tilde{\mathbb{P}}^t$ was a product of our intuition. Hence, it not a priori clear whether the fluctuations of entropy production which we can calculate through formula (29) and the measure $\tilde{\mathbb{P}}^t$ coincide with the entropy fluctuations in the original model. This problem motivates the following section.

Remark 1. However intuitive the above reasoning, one should keep in mind that we have used more information than is contained in the bare master equation (21). In particular, we used (19). To put things even sharper: given a master equation without any additional information, one could associate to it baths in different ways, thereby obtaining completely different expressions for the entropy production.

4. Linking the microscopic fluctuations with the quantum trajectory fluctuations

The idea of this section is to justify the guesses in Section 3.3. We do this by connecting fluctuations of the entropy production in the Hamiltonian model, as in expression (9) to the fluctuations calculated by the probability measure $\mathbb{P}^t_{\mu_0}$. This connection is made sharp in the regime in which the master equation is derived, i.e. in the weak coupling limit. To be as concrete as possible, we make explicit the model which was outlined in the beginning of Section 2.

Let for each k, $\mathcal{H}_k$ be a fermionic[4] Fock space, i.e.

$$\mathcal{H}_k := \mathbb{C} \oplus L^2\big(\mathbb{R}^d\big) \oplus L^2\big(\mathbb{R}^d\big) \otimes_a L^2\big(\mathbb{R}^d\big) \oplus \cdots \tag{32}$$

where the $\otimes_a$ denotes the anti-symmetrized tensor product, which accounts for the fermion statistics. Let the Hamiltonian H_k describe free fermions with one-particle dispersion relations $h_k(q) = h_k(|q|)$ where $q \in \mathbb{R}^d$ is the momentum, i.e.

$$H_k = \int_{\mathbb{R}^d} \mathrm{d}q h_k\big(|q|\big) a_k^*(q) a_k(q) \tag{33}$$

with $a_k(q), a_k^*(q)$ creators/annihilators of fermions in reservoir k with momentum q, that is

$$\big\{a_k(q), a_{k'}^*(q')\big\} = \delta_{k,k'}\delta(q-q') \tag{34}$$

Let now the interaction $H^{\mathrm{I}}_{\mathrm{S}-k}$ be given as

$$H^{\mathrm{I}}_{\mathrm{S}-k} = \int_{\mathbb{R}^d} \mathrm{d}q\ f_k(q) D_k \otimes a_k^*(q) + \bar{f}_k(q) D_k^* \otimes a_k(q) \tag{35}$$

for some operators D_k on $\mathcal{H}_{\mathrm{S}}$ and coupling functions $f_k \in L^2(\mathbb{R}^d)$. The thermal states ρ_{k,β_k} on $\mathcal{H}_k$ are defined as quasi-free states determined by their two-point correlation function (determined by the Fermi–Dirac distribution)

$$\rho_{k,\beta_k}\big[a_k^*(g') a_k(g)\big] = \big\langle g, \big(1 + \mathrm{e}^{\beta_k h_k}\big)^{-1} g'\big\rangle \tag{36}$$

We recall the definition of $F(\kappa, t, \lambda, \rho_0)$ in (9) as the Laplace transform of the distribution of entropy production:

$$F(\kappa, t, \lambda, \rho_0) = \rho_0\big[U^\lambda_{-t} \mathrm{e}^{-\kappa \sum_k \beta_k H_k} U^\lambda_t \mathrm{e}^{\kappa \sum_k \beta_k H_k}\big] \tag{37}$$

where again, as in (4), $\rho_0 = \mu_0 \otimes [\bigotimes_k \rho_{k,\beta_k}]$ with μ_0 an arbitrary density matrix on $\mathcal{H}_{\mathrm{S}}$.

We can now state the main message of this article:

> *The generating function $F(\kappa, t, \lambda, \rho_0)$ (37) from the microscopic Hamiltonian model converges in the weak coupling limit to the generating function defined by unravelings,*
>
> $$F(\kappa, t, \mu_0) = \int_{\mathbb{R}} \mathrm{d}r \mathrm{e}^{-\kappa r} \tilde{\mathbb{P}}^t_{\mu_0}\big[w^t = r\big]$$
>
> *where $\tilde{\mathbb{P}}^t_{\mu_0}$ is the measure constructed in Section 3.3. That is, under some conditions (see below) and for all $t > 0$ and initial density matrix μ_0 on $\mathcal{H}_{\mathrm{S}}$,*
>
> $$F\big(\kappa, \lambda^{-2} t, \lambda, \rho_0\big) \xrightarrow[\lambda \searrow 0]{} F(\kappa, t, \mu_0)$$

Rephrasing the fluctuation relation within the Hamiltonian model and taking $t \uparrow \infty$ one gets:

$$\lim_{t \nearrow +\infty} \lim_{\lambda \searrow 0} t^{-1} \log F\big(\kappa, \lambda^{-2} t, \lambda, \rho_0\big) = \lim_{t \nearrow +\infty} \lim_{\lambda \searrow 0} t^{-1} \log F\big(1-\kappa, \lambda^{-2} t, \lambda, \rho_0\big) \tag{38}$$

[4] One could just as well take bosons here, but then formulas like (37) need more elaboration to get rigorous meaning; see also the footnote in the introduction to Section 2.

which is a mathematical statement about large deviation generating functions.

The limit $\lambda \searrow 0$ can be omitted altogether from the above statement since the FT holds without small-coupling approximation (see [35] for a proof of existence of the limit $t \nearrow +\infty$ in that case).

These statements are essentially a rephrasing of technical results in [36], and they are more extensively commented upon in [19]. The results are proven by extending the convergence in the weak coupling limit to the full system (including reservoirs). One proves that the full Hamiltonian evolution converges to a quantum stochastic evolution. Similar results (though in a weaker form, not permitting the conclusions of this paper) have been proven in [37] and [38].

To make the discussion complete, we give an example of a set of assumptions that is sufficient to prove the above statements.

Define the set of Bohr frequencies $\mathcal{F} := \{e - e' \mid e, e' \in \mathrm{sp} H_{\mathrm{S}}\}$ and assume that:

(1) The dispersion functions $h_k : \mathbb{R}^+ \mapsto \mathbb{R}^+$ are monotone increasing, and continuously differentiable with nonzero derivative in $h_k^{-1}(\mathcal{F})$. The coupling functions f_k are also continuous in $h_k^{-1}(\mathcal{F})$. Write h_k for the self-adjoint operator associated to the dispersion function h_k by $(h_k g)(q) = h_k(|q|)g(q)$ for $g \in L^2(\mathbb{R}^d)$.

(2) For $\gamma = 0, \kappa$, the functions

$$\mathbb{R} \ni t \to \begin{cases} \rho_{k,\beta_k}[a(\mathrm{e}^{-\mathrm{i}th_k}\mathrm{e}^{-\gamma\beta_k h_k} f)a^*(f)] \\ \rho_{k,\beta_k}[a^*(\mathrm{e}^{-\mathrm{i}th_k}\mathrm{e}^{\gamma\beta_k h_k} f)a(f)] \end{cases} \tag{39}$$

are bounded and L^1-integrable.

5. Conclusion

We have investigated the question of generalization of FT to quantum systems. We remarked in Section 2.2 that in a microscopic (= Hamiltonian) framework, one can unambiguously state FT. In practice, it is more common to start from a mesoscopic (= effective, non-Hamiltonian) description of an open quantum system. In Section 3.3, we discussed a very straightforward and successful approach for the dynamics given by a specific master equation; one can guess what are fluctuations of entropy production and one can state FT. Finally, in Section 4, we state the link between fluctuations of the entropy production, defined in the microscopic model in Section 2 and the fluctuations which are the result of the guess-work in Section 3, which hence turns out to be good guess-work.

References

[1] D.J. Evans, E.G.D. Cohen, G.P. Morriss, Probability of second law violations in steady flows, Phys. Rev. Lett. 71 (1993) 2401–2404.
[2] G. Gallavotti, E.G.D. Cohen, Dynamical ensembles in nonequilibrium statistical mechanics, Phys. Rev. Lett. 74 (1995) 2694–2697.
[3] G. Gallavotti, E.G.D. Cohen, Note on two theorems in nonequilibrium statistical mechanics, J. Stat. Phys. 96 (1999) 1343–1349.
[4] C. Maes, On the origin and the use of fluctuation relations for the entropy, in: J. Dalibard, B. Duplantier, V. Rivasseau (Eds.), Poincaré Seminar, Birkhäuser, Basel, 2003, pp. 145–191.
[5] C. Maes, K. Netočný, Time-reversal and entropy, J. Stat. Phys. 111 (2003) 1219–1244.
[6] J. Kurchan, Fluctuation theorem for stochastic dynamics, J. Phys. A 31 (16) (1998) 3719–3729.
[7] J. Lebowitz, H. Spohn, A Gallavotti–Cohen type symmetry in the large deviations functional of stochastic dynamics, J. Stat. Phys. 95 (1999) 333–365.
[8] G.E. Crooks, Path ensemble averages in systems driven far from equilibrium, Phys. Rev. E 61 (2005) 2361–2366.
[9] C. Jarzynski, D. Wojcik, Classical and quantum fluctuation theorems for heat exchange, Phys. Rev. Lett. 92 (2004) 230602.
[10] J. Kurchan, Quantum fluctuation theorem, cond-mat/0007360v2.
[11] H. Tasaki, Jarzynski relations for quantum systems and some applications, Technical note, cond-mat/0009244.
[12] W. De Roeck, C. Maes, A quantum version of free energy—irreversible work relations, Phys. Rev. E 69 (2) (2004) 026115.
[13] S. Mukamel, M. Esposito, U. Harbola, Fluctuation theorem for counting-statistics in electron transport through quantum junctions, cond-mat/0702376.
[14] W. De Roeck, C. Maes, Fluctuations of the dissipated heat in a quantum stochastic model, Rev. Math. Phys. 18 (2006) 619–653.
[15] S. Mukamel, Quantum extension of the Jarzynski relation: Analogy with stochastic dephasing, Phys. Rev. Lett. 90 (2003) 170604.
[16] C.C. Marston, D. Kohen, D.J. Tannor, Phase space approach to theories of quantum dissipation, J. Chem. Phys. 107 (1997) 5236.
[17] G.S. Agarwal, Open quantum Markovian systems and microreversibility, Z. Physik 258 (1973) 409–422.
[18] R. Alicki, On the detailed balance condition for non-Hamiltonian systems, Rep. Math. Phys. 10 (2) (1976) 249–258.
[19] J. Dereziński, W. De Roeck, C. Maes, Unravelings of master equations and fluctuations of currents, cond-mat/0703594.
[20] O. Brattelli, D.W. Robinson, Operator Algebras and Quantum Statistical Mechanics 2, second ed., Springer, Berlin, 1996.

[21] J. Dereziński, Introduction to representations of canonical commutation and anticommutation relations, in: J. Derezinski, H. Siedentop (Eds.), Large Coulomb Systems – QED, Springer, 2006.
[22] V. Jakšić, Y. Ogata, C.-A. Pillet, The Green–Kubo formula and the Onsager reciprocity relations in quantum statistical mechanics, Comm. Math. Phys. 265 (2006) 721.
[23] A.E. Allahverdyan1, Th.M. Nieuwenhuizen, Fluctuations of work from quantum subensembles: The case against quantum work-fluctuation theorems, Phys. Rev. E 71 (2005) 066102.
[24] P. Talkner, E. Lutz, P. Hanggi, Fluctuation theorems Work is not an observable, cond-mat/0703189.
[25] T. Monnai, S. Tasaki, Quantum correction of fluctuation theorem, cond-mat/0308337.
[26] T. Matsui, S. Tasaki, Fluctuation theorem, nonequilibrium steady states and Maclennan–Zubarev ensembles of l^1-asymptotic abelian c* dynamical systems, Quantum Prob. White Noise Anal. 17 (2003) 100–119.
[27] I. Klich, Full counting statistics: An elementary derivation of Levitov's formula, in: Yu.V. Nazarov, Ya.M. Blanter (Eds.), Quantum Noise, Kluwer, 2003.
[28] L.S. Levitov, H. Lee, G.B. Lesovik, Electron counting statistics and coherent states of electric current, J. Math. Phys. 37 (1996) 4845–4866.
[29] J.E. Avron, S. Bachmann, G.M. Graf, I. Klich, Fredholm determinants and the statistics of charge transport, arXiv:0705.0099.
[30] R. Alicki, Invitation to quantum dynamical semigroups, in: P. Garbaczewski, R. Olkiewicz (Eds.), Dynamics of Dissipation, Lecture Notes in Physics, Springer, 2002.
[31] H.-P. Breuer, F. Petruccione, The Theory of Open Quantum Systems, Oxford Univ. Press, USA, 2002.
[32] E.B. Davies, Markovian master equations, Comm. Math. Phys. 39 (1974) 91–110.
[33] H.J. Carmichael, An Open Systems Approach to Quantum Optics, Springer, Berlin, 1993.
[34] Y.-T. Chough, H.J. Carmichael, Self-consistency of thermal jump trajectories, in: M.O. Scully, H.J. Carmichael, R.J. Glauber (Eds.), Directions in Quantum Optics, in: Lecture Notes in Physics, vol. 561, Springer, Berlin, 1999, p. 333.
[35] W. De Roeck, Large deviations for currents in the spin-boson model, arXiv:0704.3400.
[36] J. Dereziński, W. De Roeck, Stochastic limit for Pauli–Fierz operators, math-ph/0610054.
[37] R. Dümcke, Convergence of multitime correlation functions in the weak and singular coupling limits, J. Math. Phys. 24 (2) (1983) 311–315.
[38] L. Accardi, A. Frigerio, Y.G. Lu, Weak coupling limit as a quantum functional central limit theorem, Comm. Math. Phys. 131 (1990) 537–570.