**Slow Dynamics and Thermodynamics of Open Quantum Systems**

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**Abstract:** We develop a perturbation theory to estimate the finite time corrections around a quasi static trajectory, in which a quantum system is able to equilibrate at each instant with its environment. The results are then applied to non equilibrium thermodynamics, in which context we are able to provide a connection between the irreversible contributions and the microscopic details of the dynamical map generating the evolution. Turning the attention to finite time Carnot engines, we found a universal connection between the spectral density exponent of the hot/cold thermal baths and the efficiency at maximum power, giving also a new interpretation to already known results such as the Curzon-Ahborn and the Schmiedl-Seifert efficiencies.

**Keywords:** finite time thermodynamics; out of equilibrium quantum systems; irreversible processes; quantum thermodynamics; quantum control; low dissipation theory; carnot Engines

1. Introduction

An open system in contact with a thermal environment and quasistatically driven away from an initial equilibrium configuration exchanges an amount of heat that is independent from the microscopical details of the dynamics. Recognizing this universal behavior is one of the main feats of equilibrium thermodynamics, although it concerns only the ideal situation of an infinitely slow transformation and cannot provide a complete characterization of real engines. The main motivation of our analysis is to model thermodynamic processes beyond the usual reversible limit and to give a general description of the corrections to heat and work due to finite time effects.

Finite-time thermodynamics [1,2] is a well established research field which is focused on this issue and in particular on the tradeoff between efficiency and power of realistic heat engines. Several results in this context have been derived from the geometrical notion of thermodynamic length [3], from non-equilibrium identities known as fluctuation theorems [4,5], or from phenomenological models of heat engines [1,6]. The latter approach led to the identification of quite general values for the efficiency at maximum power like the Curzon-Ahborn (Chambadal-Novikov) (CA) efficiency [6–8] or the Schmiedl-Seifert (SS) efficiency [9].

We will approach the problem starting from a description of the time evolution of the system, showing that the details of the model play a role in the characterization of the irreversible corrections arising in the finite time scenario. For this sake we suppose the dynamics to be generated by a Markovian Master Equation (MME) [10,11]

\[ \dot{\rho}(t) = L_t[\rho(t)], \]  

in which \( L_t \) is the generator expressed in the Gorini-Kossakowski-Sudarshan-Lindblad (GKSL) form. The main technical innovation of the present work is the introduction of a perturbation theory...
applicable to systems slowly driven on a time scale much longer than the characteristic time of the dissipation, that allows us to provide a close formula for all the irreversible corrections in the asymptotic regime. In this way we identify a general link between the frequency scaling of the spectral density and the efficiency of finite-time Carnot heat engines, clarifying for which kind of thermal baths the Curzon-Ahlborn efficiency results or other particular limits can be recovered.

2. Results

2.1. A Slow Driving Perturbation Theory

Let us consider a driven quantum system that evolves following the Equation (1), where the explicit time dependence in $L_t$ accounts for the modulation of some external field (e.g., magnetic field). In the following we will suppose that the generator $L_t$ is relaxing, namely it has a unique instantaneous fixed point and all the other eigenvalues have a strictly negative real part. This last property implies that, given $t$, fixed, the dynamics induced by $L_t$ as a time-independent GKSL generator makes the system decay in the fixed point after a sufficiently long time, i.e.,

$$L_t[\rho] = 0 \iff \rho = \rho_0(t), \quad \lim_{t_1 \to \infty} e^{t_1 L_t}[\rho] = \rho_0(t) \quad \forall \rho. \quad (2)$$

These conditions are satisfied in a variety of systems and in particular are suitable for describing the dissipation induced by thermal environments [12–15]. Notice that for a time dependent generator the fixed point is a function of time, and we expect that for an infinitely slow driving the system follows its equilibrium configuration:

$$\rho(t) \approx \rho_0(t). \quad (3)$$

Equation (3) represents a system that is at equilibrium with its environment at every instant of time, the underlying process being a reversible transformation. In order to search the corrections to such behaviour due to finite-time effects it is convenient to introduce a rescaled time $t' \in [0,1]$ and to define accordingly $\bar{L}_t = L_{t\tau}$ and $\bar{\rho}(t') = \rho(\tau t')$. In this way the equation of motion (1) becomes $\dot{\bar{\rho}}(t') = \tau \bar{L}_{t'}[\bar{\rho}(t')]$, in which $1/\tau$ appears now as a coupling constant. The previous equation can be solved perturbatively with the following polynomial ansatz:

$$\bar{\rho}(t') = \bar{\rho}_0(t') + \bar{\rho}_1(t')/\tau + \bar{\rho}_2(t')/\tau^2 + \ldots, \quad (4)$$

which for $\tau \to \infty$ allows us to recover the quasi static solution (3). Equation (4) is not the most general solution of Equation (1) since it is independent from the initial conditions and ignores any initial exponential transient, but still approximates the asymptotic dynamics precisely (cfr. for example the numerical checks done in [16]). For a more detailed discussion we refer to [16], in which a closed formula for the $j$-th contribution of Equation (4) has also been provided, i.e., $\bar{\rho}_j(t') = [(\bar{L}_t \mathcal{P})^{-1} \frac{\partial}{\partial t'}] \bar{\rho}_0(t')$, with $\mathcal{P}$ being the projector on the traceless operator subspace.

2.2. Applications to Out of Equilibrium Thermodynamics

If the MME is generated by the contact with a thermal environment of temperature $1/\beta$, the unique instantaneous fixed point is given by the gibbs distribution $e^{-\beta H}/Z$ where $H$ is the system Hamiltonian and $Z$ is the associated partition function. In this framework the perturbative expansion (4) can be used to compute irreversible corrections to heat and work and to study the efficiency at maximum power in low dissipation carnot engines. Using a standard approach in the weak coupling regime [17–19] we identify, respectively, the mean heat absorbed by and the work done on the system in the time interval $[0,\tau]$ with

$$Q = \int_0^\tau \text{Tr}[\rho(t)H(t)]dt = \int_0^1 \text{Tr}[\bar{\rho}(t')\bar{H}(t')]dt' ; \quad W = \int_0^\tau \text{Tr}[\rho(t)\dot{H}(t)]dt = \int_0^1 \text{Tr}[\bar{\rho}(t')\dot{\bar{H}}(t')]dt'. \quad (5)$$
Since the rescaled Hamiltonian $\tilde{H}(t')$ does not depend on $\tau$ but only on the shape of the driving protocol, the $j$-th ordered correction to the heat/work in $1/\tau$ is obtained by inserting in Equation (5) the corresponding term of the expansion (4). Accordingly at the zeroth order we obtain the standard prescriptions of equilibrium thermodynamics, i.e., $Q_0 = \Delta S_0/\beta$ and $W_0 = \Delta U_0 - \Delta S_0/\beta$, where $\Delta S_0$ and $\Delta U_0$ are respectively the Von Neumann entropy and the mean energy difference between the final and initial equilibrium state. The first order corrections are instead
\[
Q_1 = \int_0^1 \text{tr} [\tilde{H}(t')\dot{\varphi}_1(t')] dt'; \quad W_1 = \Delta U_1 - Q_1,
\]
which in agreement with the second law of thermodynamics yields $Q_1 \leq 0$ [16], and confirms our expectations that in an irreversible transformation the relevant thermodynamic quantities cease to be described by universal state functions like the Helmholtz free energy or the entropy and that also the microscopic details of the dynamics play a role.

2.3. Finite Time Carnot Cycles

Let us consider a system initially at equilibrium with Hamiltonian $H_A$ and undergoing the following succession of transformations

1. Isothermal expansion: the Hamiltonian is slowly changed from $H_A$ to $H_B$, in a time interval $\tau_H$, while the system is put in contact with a hot bath of temperature $T_H$;
2. Adiabatic expansion: the Hamiltonian is suddenly changed from $H_B$ to $(T_B/T_H)H_B$;
3. Isothermal compression: The Hamiltonian is slowly changed from $(T_B/T_H)H_B$ to $(T_C/T_H)H_A$, in a time interval $\tau_C$, while the system is put in contact with a cold bath of temperature $T_C$;
4. Adiabatic compression: the Hamiltonian is suddenly changed from $(T_C/T_H)H_A$ back to $H_A$.

For a sufficiently slow driving, the heat exchanged in the isotherms can be expanded at first order in $1/\tau$ restituting the following formulas for the power and efficiency
\[
P \simeq \frac{Q_H^H + Q_I^H/\tau_H + Q_C^C/\tau_C}{\tau_H + \tau_C}, \quad \eta \simeq 1 + \frac{Q_C^C + Q_I^H/\tau_C}{Q_H^H + Q_I^H/\tau_H}.
\]

Optimizing the power over $\tau_{H,C}$ we obtain (cfr. for example [20]) the efficiency at maximum power
\[
\eta^* = \left(\frac{2}{\tau_C} - \frac{1}{1 + \sqrt{Q_C^C/Q_H^H}}\right)^{-1}.
\]

Thanks to the perturbative expansion derived in the first part of the present work we can compute the irreversible corrections $Q_H^H, Q_I^C$. Since Equation (8) appears quite difficult to compute, we assume that apart from the different time duration and a scaling factor $\beta_C/\beta_H$, the driving in the hot and cold isotherms are the time reversed of the other $\tilde{\rho}^C(t') = \tilde{\rho}^H(1 - t')$. This last hypothesis allows to derive the following universal scaling property
\[
Q_C^C/Q_H^H = (T_C/T_H)^{1-a},
\]
where $a$ is the frequency exponent of the bath spectral density $J(\omega) \approx \omega^a$, assumed to be the same for the hot and the cold baths [16]. Using the Equation (9) we can derive a universal expression for the efficiency at maximum power in the low dissipation limit
\[
\eta^* = \left(\frac{2}{1 - T_C/T_H} - \frac{1}{1 + (T_C/T_H)^{1-a}/\tau_C}\right)^{-1}.
\]

The most interesting feature of Equation (10) is that it connects a thermodynamic quantity, the efficiency at maximum power, with a microscopical, model dependent property, i.e., the spectral density of the baths. In addition, the previous formula interpolates between some celebrated results.
in the literature like the Curzon-Ahlborn efficiency and the Schmiedl Seifert efficiency, providing a unified picture and a connection of the EMP with the bath structure (as resumed in Table 1).

Table 1. Spectral density of the thermal baths and the correspектив efficiency at maximum power (EMP) in the low dissipation limit. Notice that in the case of flat and ohmic spectral densities we recover respectively the CA and the SS efficiencies.

| Flat Bath | Ohmic Bath | Infinitely Super Ohmic Bath | Infinitely Sub Ohmic Bath |
|-----------|------------|-----------------------------|--------------------------|
| $J(\omega) = \Gamma \omega$ | $J(\omega) = \Gamma \omega$ | $J(\omega) = \Gamma \omega^{\alpha \to \infty}$ | $J(\omega) = \Gamma \omega^{\alpha \to -\infty}$ |
| $\eta^\ast|_{\alpha=0} = 1 - \sqrt{\frac{T_c}{T_h}}$ | $\eta^\ast|_{\alpha=1} = \frac{2\pi}{z^\alpha}$ | $\eta^\ast|_{\alpha=1} = \frac{2\pi}{z^\alpha}$ |

3. Discussion

We have introduced a perturbative expansion for describing the evolution generated by a MME with slowly varying parameters. Applying this technique to finite time engines we establish a new universal connection between the EMP and the spectral density of the hot and cold baths.

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