Slow Dynamics and Thermodynamics of Open Quantum Systems

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We develop a perturbation theory of quantum (and classical) master equations with slowly varying parameters, applicable to systems which are externally controlled on a time scale much longer than their characteristic relaxation time. We apply this technique to the analysis of finite-time isothermal processes in which, differently from quasistatic transformations, the state of the system is not able to continuously relax to the equilibrium ensemble. Our approach allows one to formally evaluate perturbations up to arbitrary order to the work and heat exchange associated with an arbitrary process. Within first order in the perturbation expansion, we identify a general formula for the efficiency at maximum power of a finite-time Carnot engine. We also clarify under which assumptions and in which limit one can recover previous phenomenological results as, for example, the Curzon-Ahlborn efficiency.

A central result in the study of open quantum systems [1,2] is the Markovian master equation (MME) approach which, under realistic assumptions, describes the temporal evolution of a system of interest A induced by a weak coupling with a large external environment E. This consists in a first order linear differential equation $\dot{\rho}(t) = \mathcal{L}[\rho(t)]$, where $\rho(t)$ is the density matrix of A and where the generator of the dynamics is provided by a quantum Liouvillian superoperator $\mathcal{L}$ that can be casted in the so-called Gorini-Kossakowski-Sudarshan-Lindblad form [3–5]. For autonomous systems the latter does not exhibit an explicit time dependence and the dynamics of A exponentially relaxes to a (typically unique) equilibrium steady state ρ_0 identified by the null eigenvector equation $\mathcal{L}[\rho_0] = 0$. MMEs can also be employed to describe the temporal evolution of A when it is tampered by the presence of slow varying, external driving forces. Indeed, as long as these operate on a time scale which is much larger than the characteristic bath correlation times and the inverse frequencies of the system of interest, the effective coupling between A and E adapts instantaneously to the driving control, resulting on a MME governed by a time-dependent Liouvillian generator, i.e.,

$$\dot{\rho}(t) = \mathcal{L}_t[\rho(t)]. \tag{1}$$

An explicit integration of this equation is in general difficult to obtain. Yet, if the control forces are so slow that their associated time scale is also larger with respect to the relaxation time of the system induced by the interaction with E, one expects $\rho(t)$ to approximately follow the instantaneous equilibrium state $\rho_0(t)$ that nullifies $\mathcal{L}_t$. Our aim is to estimate quantitative deviations from this ultraslow driving regime. For this purpose we develop a perturbation theory valid in the limit of slowly varying Liouvillians $\mathcal{L}_t$ and derive a formal solution of Eq. (1) which allows one to evaluate nonequilibrium corrections up to arbitrary order.

The main motivation of our analysis is to model thermo-dynamic processes and cycles beyond the usual reversible limit which is strictly valid only for infinitely long quasi-static transformations. Finite-time thermodynamics [6,7] is a well-established research field that is focused on this issue and, in particular, on the trade-off between efficiency and power of realistic heat engines. Several results in this context have been derived from the geometrical notion of thermodynamic length [8], from nonequilibrium identities known as fluctuation theorems [9,10], or from phenom-enological models of heat engines [6,11]. The latter approach led to the identification of a quite general value for the efficiency at maximum power which is the celebrated Curzon-Ahlborn (Chambadal-Novikov) efficiency [11–13]. Our framework is complementary to previous approaches since it allows one to explicitly express irreversible thermo-dynamic quantities (e.g., heat and work) in terms of the Liouvillian operator that governs the system dynamics. 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 result or other particular limits can be recovered.

Similar questions and problems have been addressed in the literature with different aims and methods. Finite-time quantum thermodynamics [14–16] and Brownian quantum engines [17,18] were studied using the formalism of open quantum systems. In particular single-qubit heat engines subject to Markovian dissipation were considered in Refs. [19–22]. The impact of the bath spectral density on the efficiency of quantum engines was also noticed in the context of autonomous heat pumps [23,24] and single-qubit minimal machines [25]. Universal features and bounds for the efficiency at maximum power of finite-time Carnot cycles were identified in Refs. [17,26–28] for generic heat engines. Other results were obtained combin-ing MMEs and linear response theory [6,29,30] and similar approaches were used to demonstrate the universality of heat engines in the limit of infinitesimal cycles [31].

Outside the field of thermodynamics, our theory of slowly driven open quantum systems also contributes to the current research activity on quantum adiabatic driving. Several generalizations of the adiabatic theorem to open quantum systems have been already proposed [30,32–34]. Our aims and results are, however, different: we are not interested in the derivation of a modified MME for time-dependent Hamiltonians but only on the dynamical evolution of A for an assigned time-dependent Liouvillian $\mathcal{L}_t$ that, for all t, admits a unique (instantaneous) equilibrium state. This kind of adiabatic approach has recently proved to be effective in the study of general time-dependent Liouvillians with higher dimensional kernels [35–37]. We finally would like to stress that, by replacing $\rho(t)$ with a probability vector, all the results that we are going to present in the following are directly applicable also to classical continuous-time Markov processes [38].

Slow driving perturbation theory.—Let us consider the case of an open quantum system A evolving as in Eq. (1) under the action of a quantum Liuovillian $\mathcal{L}_t$ which exhibits an explicit temporal dependence induced by the external modulation of some control parameters, say the value of a magnetic field or the intensity of a laser which are gradually changed according to some assigned protocol. In what follows we shall assume that for all t, $\mathcal{L}_t$ admits a unique zero (instantaneous) eigenstate $\rho_0(t)$ and that all the other eigenvalues have a strictly negative real part (in this case the map is said to be relaxing or mixing [2,39]). This causes the system to exponentially converge to the instantaneous steady state, for a fixed value of the external modulation:

$$\text{Assumption 1:}\quad \lim_{s\to\infty} e^{\mathcal{L}_t s}[\rho] = \rho_0(t), \quad \forall\, \rho, t. \quad (2)$$

Under these conditions, one can easily verify that for an infinitely slow modulation of $\mathcal{L}_t$, the system A will be forced to follow quasistatically the trajectory determined by the time-dependent density matrix $\rho_0(t)$, i.e.,

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

Physically this follows from the fact that, in this regime, there is enough time for A to track the instantaneous equilibrium states defined by $\mathcal{L}_t$. This solution well approximates the dynamics of realistic configurations where, for instance, the system of interest is in thermal contact with a reservoir while being subject to a quasistatic external control, continuously relaxing to the instantaneous Gibbs ensemble. Notice, however, that at this stage of the analysis $\rho_0(t)$ can be an arbitrary quantum state, covering more general open evolutions including also systems in contact with engineered nonthermal baths (e.g., squeezed environments, negative temperatures, artificial dissipative maps, etc.). To characterize deviations from the quasistatic solution, Eq. (3), we find it convenient to introduce the following time-rescaled quantities

$$\tilde{\mathcal{L}}_{t'} = \mathcal{L}_{\tau t'}, \qquad \tilde{\rho}(t') = \rho(\tau t'), \quad (4)$$

where τ is the duration of the protocol, i.e., the total time interval on which the system evolves under the influence of the external control. With this choice Eq. (1) can be expressed as

$$\dot{\tilde{\rho}}(t') = \tau\tilde{\mathcal{L}}_{t'}[\tilde{\rho}(t')], \quad (5)$$

the dynamics being confined now into the unit interval $t' \in [0,1]$. In this way the total duration of the protocol appears only as a multiplicative factor while all the information about its "shape" is contained in $\tilde{\mathcal{L}}_{t'}$. Notice also that while $\tilde{\mathcal{L}}_{t'}$ is independent of τ, the time-rescaled solution $\tilde{\rho}(t')$ of Eq. (5) is not. In particular the quasistatic solution (3) can be recovered from Eq. (5) in the asymptotic limit $\tau \to \infty$. Therefore, we look for a perturbation expansion of the solution of Eq. (5) in powers of $1/\tau$:

$$\tilde{\rho}(t') = \tilde{\rho}_0(t') + \frac{\tilde{\rho}_1(t')}{\tau} + \frac{\tilde{\rho}_2(t')}{\tau^2} + \cdots, \quad (6)$$

where normalization implies that all perturbations are traceless:

$$\text{tr}[\tilde{\rho}_j(t')] = 0, \quad \forall\, j > 0. \quad (7)$$

A rigorous mathematical analysis of the convergence properties of the series (6) is beyond the aim of this work. For our purposes it is sufficient that Eq. (6), truncated up to a finite order, provides a good approximation of the dynamics. The validity of this approach is verified in several numerical examples presented in the Supplemental Material (Appendixes A, B, and C) [40].

Substituting Eq. (6) in both sides of Eq. (5), and equating the terms proportional to same powers of $1/\tau$, we get the following set of recursive relations:

$$0 = \tilde{\mathcal{L}}_{t'}[\tilde{\rho}_0(t')], \quad (8)$$

$$\dot{\tilde{\rho}}_j(t') = \tilde{\mathcal{L}}_{t'}[\tilde{\rho}_{j+1}(t')], \qquad j = 0, 1, \ldots. \quad (9)$$

As expected, Eq. (8) implies that $\tilde{\rho}_0(t')$ is the (time-rescaled) instantaneous steady state of the Liouvillian. Moreover, from Eq. (9), all finite-time perturbations can be recursively obtained. Indeed, exploiting Eq. (7), Eq. (9) can be univocally inverted by introducing the projector $\mathcal{P}$ on the traceless subspace, i.e., $\mathcal{P}[X] = X - \text{tr}(X)\mathbb{I}/d$ with $\mathbb{I}$ being the identity operator on A and d the dimension of its Hilbert space. Now since $\text{tr}[\rho_0(t)] = 1 \neq 0$, the Liouvillian within the subspace of traceless operators is invertible and we also have $(\mathcal{P}\mathcal{L}_t\mathcal{P})^{-1} = (\mathcal{L}_t\mathcal{P})^{-1}$. Accordingly, for all j we can write Eq. (9) as $\tilde{\rho}_{j+1}(t') = (\tilde{\mathcal{L}}_{t'}\mathcal{P})^{-1}\dot{\tilde{\rho}}_j(t')$, which by iteration yields explicit formulas for each perturbative term:

$$\tilde{\rho}_j(t') = \left((\tilde{\mathcal{L}}_{t'}\mathcal{P})^{-1}\frac{d}{dt'}\right)^j \tilde{\rho}_0(t'). \qquad (10)$$

Switching from time-rescaled variables back to the original ones, the full solution of the MME can be compactly expressed as an operator geometric series:

$$\rho(t) = \frac{1}{1 - (\mathcal{L}_t\mathcal{P})^{-1}\frac{d}{dt}}\rho_0(t). \qquad (11)$$

It is worth stressing that the above solution is unique and independent on the initial conditions. This is due to the fact that, at this level of approximation, we are neglecting any term exponentially decaying in τ. In other words, the perturbations that we are considering are intrinsic to the Liouvillian operator without any influence from the initial state. In practice this means that all exact solutions of the master equation, after an exponentially short transient depending on the initial conditions, will converge to the asymptotic solution (11). This is a fundamental difference with respect to the Hamiltonian adiabatic theorem in which finite-time corrections depend on initial conditions and decay exponentially in τ. In the next sections we present a couple of relevant applications of the results presented above to the context of finite-time thermodynamics.

Finite-time isothermal process.—Let us consider the case of a thermal MME, Eq. (1), describing the dynamical evolution of A induced by an external driving that slowly modifies its Hamiltonian $H(t)$ while the system is constantly kept in thermal contact with a bath of fixed inverse temperature β. In this scenario the instantaneous equilibrium state of the problem can be identified with the Gibbs density matrix $\rho_0(t) = \exp[-\beta H(t)]/Z(t)$, with $Z(t) = \mathrm{tr}\{\exp[-\beta H(t)]\}$ being the associated partition function. Exploiting the derivation of the previous section we wish to determine how departures from the associated quasistatic trajectory, Eq. (3), influence the thermodynamic properties of the process. For this purpose we note that the mean energy and the von Neumann entropy of A are given by $U(t) = \mathrm{tr}[H(t)\rho(t)]$ and $S(t) = -\mathrm{tr}\{\rho(t)\log[\rho(t)]\}$, respectively. Moreover, following a common approach [14,15,41,42] we identify the mean heat absorbed by the system during the time interval $[0,\tau]$ with

$$Q = \int_0^\tau \mathrm{Tr}[\dot{\rho}(t)H(t)]dt = \int_0^1 \mathrm{Tr}[\dot{\tilde{\rho}}(t')\tilde{H}(t')]dt', \qquad (12)$$

and the mean work done on the system with

$$W = \int_0^\tau \mathrm{Tr}[\rho(t)\dot{H}(t)]dt = \int_0^1 \mathrm{Tr}[\tilde{\rho}(t')\dot{\tilde{H}}(t')]dt', \qquad (13)$$

such that the first law of thermodynamics is obtained as $\Delta U = U(\tau) - U(0) = W + Q$. Now, since the time-rescaled Hamiltonian $\tilde{H}(t')$ does not depend on τ but only

on the shape of the protocol, all the previous quantities are influenced by τ only through the solution of the master equation $\rho(t)$, for which we know how to evaluate each perturbative term of the series (6). Therefore, we can write $X = X_0 + X_1/\tau + X_2/\tau^2 + \cdots$ with $X = U, S, W, Q$, and we can easily evaluate each term using Eq. (10). For example, at the zeroth order approximation we recover the standard results of equilibrium thermodynamics: $U_0(t) = -(\partial/\partial\beta)\log Z(t)$, $S_0(t) = [1 - (\partial/\partial\beta)]\log Z(t)$, $Q_0 = \Delta S_0/\beta$, and $W_0 = \Delta U_0 - \Delta S_0/\beta$. The corresponding first order irreversible corrections are instead

$$U_1(t) = \mathrm{tr}[\tilde{H}(t')\tilde{\rho}_1(t')]|_{t'=t/\tau}, \qquad (14)$$

$$S_1(t) = -\mathrm{Tr}[\tilde{\rho}_1(t')\log(\tilde{\rho}_0(t'))]|_{t'=t/\tau} = \beta U_1(t), \qquad (15)$$

$$Q_1 = \int_0^1 \mathrm{tr}[\tilde{H}(t')\dot{\tilde{\rho}}_1(t')]dt', \qquad (16)$$

$$W_1 = \Delta U_1 - Q_1, \qquad (17)$$

with $\tilde{\rho}_1(t)$ as in Eq. (10). It is worth noticing that, independently from the selected form of the MME, the first law of thermodynamics is valid at the level of each perturbative coefficient $\Delta U_j = W_j + Q_j$ and that, for an initial Gibbs state $\rho(0) = \rho_0(0)$, the second law can be expressed as $Q \leq Q_0$ or, equivalently, as $W \geq W_0$. Taking the limit of large τ, this implies that $Q_1 \leq 0$ and $W_1 \geq 0$. Moreover, if we consider the time-reversed process $\tilde{\mathcal{L}}_{t'}^{\leftarrow} = \tilde{\mathcal{L}}_{1-t'}$, then it is easy to check that odd-order perturbations are invariant while even-order perturbations change sign $Q_j^{\leftarrow} = (-1)^{j+1}Q_j$ and $W_j^{\leftarrow} = (-1)^{j+1}W_j$.

Finite-time Carnot cycles.—As a second application of our slow driving perturbative approach consider the case where A, initialized in a Gibbs state with Hamiltonian H_A, evolves following a Carnot cycle composed by (1) Isothermal expansion: the system is put in contact with a hot bath of temperature T_H and the Hamiltonian is slowly changed from H^A to H^B, in a time interval τ_H. (2) Adiabatic expansion: the Hamiltonian is suddenly changed from H^B to $(T_C/T_H)H^B$. (3) Isothermal compression: the system is put in contact with a cold bath of temperature T_C and the Hamiltonian is slowly changed from $(T_C/T_H)H_B$ to $(T_C/T_H)H_A$, in a time interval τ_C. (4) Adiabatic compression: the Hamiltonian is suddenly changed from $(T_C/T_H)H_A$ back to H_A.

The scaling factor T_C/T_H characterizing the adiabatic operations is chosen to ensure that the stationary (Gibbs) state $\rho_0(t)$ evolves continuously in time during the cycle such that, for infinitely long processes, the system remains always in equilibrium without irreversible jumps. In addition to this standard requirement we also assume that $\rho_0(t)$ is sufficiently smooth, so that all the derivatives appearing in our perturbation theory are well defined along the cycle. Specifically, since in what follows we are going to consider

only first-order perturbations, we assume the following:
Assumption 2: $\rho_0(t)$ is continuous and differentiable.

We also assume that, apart from the Hamiltonian scaling factor T_C/T_H and its time length, the cold isothermal protocol is the time reversal of the hot one: $\tilde{H}^C(t') = (T_C/T_H)\tilde{H}^H(1-t')$. In terms of the associated time-rescaled Gibbs states, this is equivalent to

$$\text{Assumption 2:}\quad \tilde{\rho}^C(t') = \tilde{\rho}^H(1-t'). \qquad (18)$$

The latter assumption is common in many realistic heat engines and can be relaxed if we are free to optimize the shape of the two isothermal processes. Indeed in this case, within first order in the perturbation expansion that we are going to present later, the maximum output power is obtained when the driving protocol respects the time-reversal symmetry condition (18).

Now we are ready to analyze the performances of our finite-time Carnot engine. In the limit of many cycles the system evolution becomes periodic ($\Delta U = 0$) and the work per cycle depends only on the heat exchanged in the hot and cold isothermal processes: $W = -Q^H - Q^C$. The power is the ratio between the work extracted and the time length of the cycle $P = -W/(\tau_H + \tau_C) = (Q^H + Q^C)/(\tau_H + \tau_C)$, while the thermodynamic efficiency is defined as $\eta = -W/Q^H = 1 + Q^C/Q^H$. If we substitute the perturbative expansion, keeping only first-order terms in τ_H and τ_C, we obtain

$$P \simeq \frac{Q_0^H + Q_1^H/\tau_H + Q_0^C + Q_1^C/\tau_C}{\tau_H + \tau_C}, \qquad (19)$$

$$\eta \simeq 1 + \frac{Q_0^C + Q_1^C/\tau_C}{Q_0^H + Q_1^H/\tau_H}. \qquad (20)$$

In the quasistatic limit $\tau_C, \tau_H \to \infty$, the power tends to zero and the efficiency reaches the Carnot limit

$$\eta_C = 1 + Q_0^C/Q_0^H = 1 - T_C/T_H. \qquad (21)$$

The power can be maximized with respect to τ_H and τ_C, taking into account the physical constraints $Q_0^H > 0$, Q_0^C, Q_1^H, $Q_1^C < 0$. The corresponding efficiency at maximum power can be easily computed (see, e.g., Ref. [17]):

$$\eta^* = \left[\frac{2}{\eta_C} - \frac{1}{1 + \sqrt{Q_1^C/Q_1^H}}\right]^{-1}. \qquad (22)$$

We also notice that, in the particular case in which heat corrections are proportional to the temperature, Eq. (22) reduces to the efficiency derived in Ref. [26].

We can now make use of Eqs. (16) and (10) to express both Q_1^H and Q_1^C in terms of the Liouvillians $\mathcal{L}_{t'}^H$ and $\mathcal{L}_{t'}^C$ describing the two isothermal processes. Both irreversible

heat corrections depend on the particular choice of the protocol, however, we find that their ratio has the following scaling:

$$Q_1^C/Q_1^H = (T_C/T_H)^{1-\alpha}, \qquad (23)$$

where α is the frequency exponent of the bath spectral density $J(\omega) \propto \omega^\alpha$, which is assumed to be the same for both the hot and the cold reservoirs. The proof of Eq. (23) can be found in the Supplemental Material (Appendix D) [40] and follows from the time-reversal condition (18) and a general scaling property characterizing all MMEs obtained from standard microscopic models. Substituting Eq. (23) in Eq. (22), we get our final result (see Fig. 1 for a plot):

$$\eta^* = \left[\frac{2}{1 - T_C/T_H} - \frac{1}{1 + (T_C/T_H)^{(1-\alpha)/2}}\right]^{-1}. \qquad (24)$$

The peculiarity of the universal expression (24) is that, by changing the parameter α, it interpolates between several results that were previously obtained in the literature. For example, for a flat spectral density ($\alpha = 0$), we recover the Curzon-Ahlborn [11–13] efficiency $\eta^*|_{\alpha=0} = 1 - \sqrt{T_C/T_H}$, while for an Ohmic bath $\alpha = 1$ we get $\eta^*|_{\alpha=1} = 2\eta_C/(4 - \eta_C)$, which is the efficiency obtained by Schmiedl and Seifert for a specific Brownian engine [17]. Finally, consistently with known lower and upper bounds [6,17,26], by taking the two limits of the infinitely super-Ohmic or sub-Ohmic bath, we get $\eta^*|_{\alpha\to\infty} = \eta_C/2 \le \eta^* \le \eta_C/(2 - \eta_C) = \eta^*|_{\alpha\to-\infty}$.

In Refs. [23–25], the efficiency of minimal models of heat engines and refrigerators was also linked to the spectral density. Such models are quite different from the Carnot cycles considered in this work but still one can find a qualitative agreement with our results.
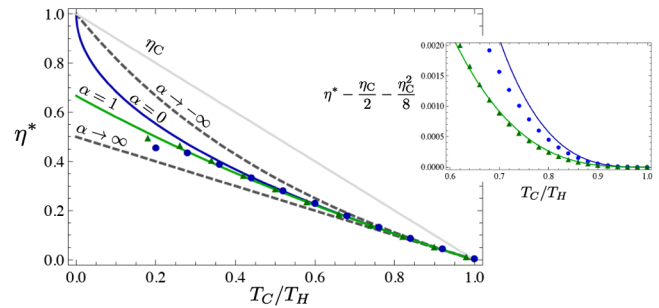

FIG. 1. Efficiency at maximum power η^* with respect to the temperature ratio T_C/T_H for different values of the spectral density exponent α; see Eq. (24). Light gray line represents the Carnot bound; blue circles and green triangles are exact numerical results based on a two-level system heat engine coupled to a flat ($\alpha = 0$) and Ohmic bath ($\alpha = 1$), respectively. The details of the simulation are reported in the Supplemental Material (Appendix C) [40].

A final remark should be made on the range of applicability of Eq. (24). Its derivation follows from the first order expansion performed in Eqs. (19) and (20), which is not guaranteed to be always valid in the regime of maximum power, especially for $T_C/T_H \simeq 0$, where the optimal values of τ_H and τ_C could become too small. This is confirmed by the single-qubit exact simulation shown in Fig. 1, where we observe deviations from Eq. (24) for small values of T_C/T_H. It is interesting then to expand Eq. (24) around the opposite regime, i.e., for small values of $\eta_C = 1 - T_C/T_H$, obtaining

$$\eta^* = \eta_C/2 + \eta_C^2/8 + \eta_C^3(2-\alpha)/32 + O(\eta_C^4). \quad (25)$$

We notice that the first and second order coefficients, (i.e., 1 and 1/8) are independent of α and correspond to the same values in the Taylor expansion of the Curzon-Ahlborn [11,20] and of the Schmiedl-Seifert [17] efficiencies. This also implies that, up to second order in η_C, our results are in agreement with previous analyses based on linear response thermodynamics [6,28].

Conclusions and outlook.—We have derived a perturbation theory for the solution of generic master equations with slowly varying coefficients. We focused, in particular, on finite-time thermodynamic processes beyond the reversible limit. Our analysis allows us to analytically derive finite-time thermodynamic quantities in terms of the Liouvillian operator. We have also shown that, for a Carnot cycle, the efficiency at maximum power can be reduced to a universal formula depending only on the temperature ratio and on the scaling of the bath spectral density. Other implications of the perturbation theory presented in this work could also be studied in the future, in particular within the general context of quantum adiabatic driving.

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