

Open quantum systems coupled to time-dependent classical environments

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Abstract We investigate the behavior of open quantum systems interacting with classical time-dependent environments. As a simple example of a quantum system we employ a two-level quantum system, and a thermodynamic oscillator serves as an environment. We analyse how the relationship between parameters of the classical environment and the quantum subsystem changes the evolution. Using the nonlinear thermodynamic master equation we demonstrate how the energy and the coherence of the quantum system evolve in time and how effects of a feedback from a quantum to a classical system influences its dynamics.

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1 Introduction

In recent years there has been a growing interest in the physics of open quantum systems. It is of crucial importance for understanding and developing the quantum computer [1]. Also it is widely used in a field of quantum optics [2],

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transport phenomena [3,4], the theory of photosynthetic complexes [5] and even for the theory of a gravity [6].

The main idea of the theory is very simple: we investigate the dynamics of only the small quantum system of interest, whereas all other degrees of freedom are considered to be an environment, dynamics of which is included implicitly [7]. This approach simplifies calculations a lot, instead of solving the Schrödinger equation for $\propto 10^{27}$ quantum particles, one has to solve so-called master equation only for few of them, which dynamics is the most important.

The problem that arises: how should the environment be treated? Usually it is stated that the environment consists of an infinite number of quantum harmonic oscillators which do not interact between of each other [8]. However, this so-called harmonic bath assumption is still unjustified [9]. The second approach, which is widely used in chemistry (vibrational relaxations in liquids, electron and proton transfer etc.), deals with the environment as a classical mechanical system [10]. The relaxation rates are calculated with the help of molecular dynamics. This method is very powerful but it requires serious computational calculations. Therefore, we suggest to discuss a more coarse-grained version of the environment and apply methods of modern nonequilibrium thermodynamics [11] to it. We would like to describe a classical environment as a thermodynamic system and investigate the interaction between quantum system and environment using the nonlinear thermodynamic master equation [12,13].

In this article we review the nonlinear thermodynamic master equation. With a simple example (Fig. 1) we show how the time-dependence of the environment changes the dynamics of a quantum system. Also we show how the reaction of the quantum system on the classical environment can be quantified.

The plan of this paper is as follows: in Sec. 2, we describe our tool for investigating quantum-classical dynamics — the nonlinear thermodynamic master equation which describes the evolution of a density matrix of a quantum system. In addition, we formulate a feedback equation which quantifies how the quantum system affects the classical one. In Sec. 3, we describe the two-level quantum system, introduce the most important definitions from quantum mechanics, and show the energy relaxation of a quantum system coupled to a heat bath. Also the thermodynamic oscillator is introduced here and its behavior is analyzed. In Sec. 4, we show the main results for a two-level quantum system coupled to the thermodynamic oscillator. Finally we discuss our results and give conclusions.

2 Nonlinear thermodynamic master equation

Quantum master equations are useful tools for exploring open quantum systems [7,14] and are usually assumed to have a linear form (e.g. Lindblad form [15,16])

$$\frac{d\rho}{dt} = -i\mathcal{L}\rho, \quad (1)$$

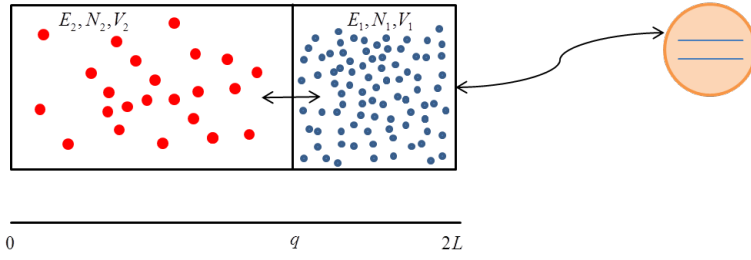


Fig. 1 Model of quantum system coupled to time-dependent thermodynamic environment.

where \mathcal{L} is a superoperator. However two-time correlation functions of two observables calculated with the “quantum regression hypothesis” and the fluctuation-dissipation theorem of the first kind are different. This means that the linear form of the superoperator causes the failure of the “quantum regression hypothesis” for quantum dissipative systems [13, 17, 18]. Motivated by this fact, Grabert derives a nonlinear master equation which, in the Markovian limit, has the following form [18]

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{M}{k_B T_e} [Q, [Q, H]\rho] - M[[Q, [Q, \rho]], \quad (2)$$

with a suitable parameter M describing the strength of the dissipation and an observable Q describing the interaction between quantum subsystem and its infinite quantum environment. The temperature T_e is the only parameter characterizing the state of the environment, which hence acts as a heat bath.

Recently, the nonlinear master equation was generalized to more complicated classical nonequilibrium systems as environments. Based on purely thermodynamic considerations and a generalization from classical to quantum systems inspired by a geometric formulation of nonequilibrium thermodynamics, the following master equation for the evolution of the density matrix or statistical operator ρ has been proposed [12, 13]

$$\frac{d\rho}{dt} = \frac{i}{\hbar}[\rho, H] - \frac{1}{k_B} [H_e, S_e]_x^Q [Q, [Q, H]\rho] - [H_e, H_e]_x^Q [Q, [Q, \rho]]. \quad (3)$$

It is important to note that (3) characterizes a quantum subsystem in contact with an arbitrary classical nonequilibrium system acting as its environment. The first term describes the free evolution generated by the Hamiltonian H and two other terms have irreversible nature and are caused by coupling a quantum subsystem to its environment. Whereas the type of coupling is given by the self-adjoint coupling operator Q , the strength of the coupling is expressed in a dissipative bracket $[\cdot, \cdot]_x^Q$ defined as a binary operation on the space of observables for the classical environment. If the equilibrium or nonequilibrium states of the environment are characterized by the state variables x , classical observables are functions or functionals of x which is indicated

by subscript. The classical observables H_e and S_e in eq. 3 are the energy and the entropy of the environment, respectively. Properties of dissipative brackets are explained in details in [13]. In our work we will use following form of dissipative brackets

$$[A_e, B_e]^Q = \frac{dA_e}{dH_e} M(T_e) \frac{dB_e}{dH_e}, \quad (4)$$

where $M(T_e)$ is a positive function of a temperature of environment and defined later.

The master equation (3) describes the influence of a classical environment on a quantum subsystem. Of course, in response the quantum system also has an influence on its environment. The thermodynamic approach provides a corresponding equation for the evolution of environmental observables,

$$\begin{aligned} \frac{dA_e}{dt} = \left(\frac{dA_e}{dt} \right)_{\text{class}} - \frac{1}{k_B} [A_e, S_e]_x^Q \langle [Q, H]; [Q, H] \rangle_\rho \\ + [A_e, H_e]_x^Q \langle [Q, [Q, H]] \rangle_\rho. \end{aligned}$$

where canonical correlations are given

$$\langle A; B \rangle_\rho = \int_0^1 \text{tr}(\rho^\lambda A \rho^{1-\lambda} B) d\lambda = \text{tr}(A_\rho B). \quad (5)$$

To integrate the nonlinear thermodynamic master equation we apply the fourth-order RungeKutta method according to the procedure described in [13]. Alternatively, stochastic simulation technique [19] has been developed and can be applied.

3 Models of quantum system and classical environment

Quantum system. The two-level system is the simplest quantum system and it has two possible quantum states. Many areas of a modern science use this simple model. Examples from a quantum chemistry include the electron and proton transfer as well as isomerization reactions. In a quantum optics the model successfully describes nuclear magnetic resonance and spontaneous emission. In quantum computing it is called “qubit”, and two states are accordingly denoted $|0\rangle$ and $|1\rangle$.

Any two-dimensional Hermitian matrix of trace one can serve as a density matrix of two-level system. It is fully defined by three parameters. Hence, one can always write the density matrix of a any (mixed or pure) state of the two-level system as

$$\rho = \frac{1 + m_1 \sigma_1 + m_2 \sigma_2 + m_3 \sigma_3}{2} = \frac{1 + \mathbf{m} \cdot \boldsymbol{\sigma}}{2}, \quad (6)$$

where the σ_i are the Pauli matrices.

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \quad (7)$$

The vector \mathbf{m} which is used to parametrize the density matrix is called the Bloch vector. In addition to conserving the trace equal to one, the density matrix is positive semi-definite, which restricts the length of a Bloch vector $m \leq 1$, where equality holds only for case of a pure state. The expectation value for any observable A is given by

$$\langle A \rangle = \text{tr}(\rho A), \quad (8)$$

therefore information about the dynamics of the Bloch vector allows to describe the dynamics of any observable. Hence, our main goal is to find the evolution of m . The initial values of the Bloch vector are following: $m_1 = 0.0$, $m_2 = 0.4$, $m_3 = 0.5$. Firstly, we demonstrate an evolution equation of a quantum system coupled to a heat bath. As a Hamiltonian of a two-level system we choose $H = \frac{1}{2}\hbar\omega\sigma_3$, where ω is the angular frequency associated with the energy difference between two levels of the system. Two coupling operators as defined as $Q_j = \sigma_j$, where $j = 1, 2$. The heat bath is characterised by its energy H_e and the temperature is implied by the thermodynamic relationship $S_e(H_e)$. We assume dissipative brackets of the form

$$[A_e, B_e]_{H_e}^{Q_j} = \frac{dA_e}{dH_e} \gamma_0 \frac{k_B}{T_e} \frac{dB_e}{dH_e}. \quad (9)$$

The energy of a qubit is proportional to the $m_3 = \langle \sigma_3 \rangle$ and its relaxation caused by coupling to a heat bath is shown in Fig. 2. In case of any temperature of a heat bath there is always monotonic behavior of the curve. The final value of energy of a quantum system coupled to a heat bath is defined by the Gibbs distribution.

To understand typical values of energies and work with dimensionless units we discuss superconducting qubits [20]. The frequency of transitions between the excited and the ground state ω_{exp} is of order of 10 GHz. In our simulations we work with $\omega \propto 10$ that means that one dimensionless unit of time [t] $\propto \frac{\omega}{\omega_{\text{exp}}} = 10^{-10}$ [s]. One unit of temperature in Hz is [T] $\propto \frac{\omega_{\text{exp}}}{\omega} = 10^9$ [Hz]. Recalling that 1 K corresponds to about 20 GHz, one dimensionless unit of temperature can be written [T] $\propto 0.5 \cdot 10^{-10} \frac{\omega_{\text{exp}}}{\omega} = 0.05$ [K].

Classical environment. Now we discuss the simplest possible example of a nonequilibrium thermodynamic environment. It consists of two subsystems exchanging heat and volume through a separating wall of mass m (see Fig. 1 left side). We use $x = (q, v, E_1, E_2)$ as variables for the system, where v is the velocity of the wall. For our simulations we assume that initially the wall is at rest ($v = 0$). Assuming that the subsystems contain the same number of particles $N_1 = N_2 = N$ we can derive time-evolution equations describing the system [21]

$$\frac{dq}{dt} = v, \quad (10)$$

$$\frac{dv}{dt} = \frac{1}{m}(p_1 - p_2)A_c, \quad (11)$$

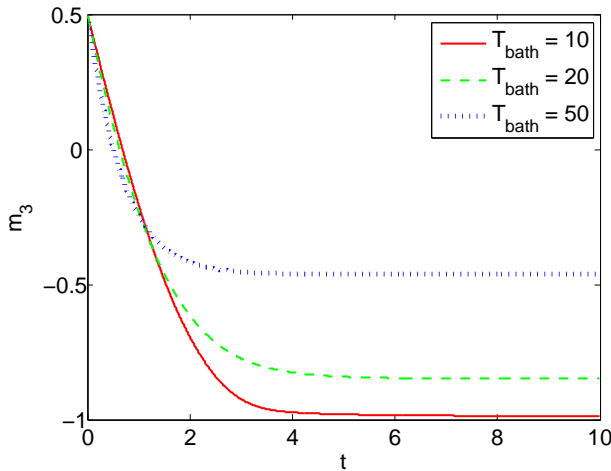


Fig. 2 Relaxation of energy of a two-level quantum system coupled to a heat bath. Temperature changes only the slope of the decay which is always monotonic.

$$\frac{dE_1}{dt} = -p_1 A_c v + \alpha \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (12)$$

$$\frac{dE_2}{dt} = p_2 A_c v - \alpha \left(\frac{1}{T_1} - \frac{1}{T_2} \right), \quad (13)$$

where the parameter α is responsible for the heat exchange between the two volumes. Energy and pressure of the subsystems are functions of temperature and volume. In order to show some numerical results we can apply ideal gas laws and solve the closed system of equations. However, it should be mentioned that (10-13) are valid for any real system inside the two volumes. For more complicated models we can not obtain an analytical system of equations and should perform simulations.

Depending on the values of initial temperatures, heat exchange and other parameters, there exist two different kind of solutions of (10-13). The temperatures of the subsystems can either change monotonically or show damped oscillations. The typical patterns are shown in Fig. 3.

Quantum-classical coupling The coupling a quantum system to the thermodynamic oscillator is shown in Fig. 1. The quantum system interacts only with the volume which has the energy E_1 . In addition, the volume V_2 knows about the quantum system through the wall. The dynamics of our coupled quantum-classical system is defined by many parameters and variables. The evolution of the classical environment plays an important role, however, the relationship between certain parameters of systems is even more important. The first such ratio is $\beta_1 = \frac{\gamma}{\alpha}$ which shows how different the quantum and classical coupling are; the second parameter $\beta_2 = \frac{m}{Nm_p}$, where m is a mass of a wall between the two volumes and Nm_p is a total mass of the volumes.

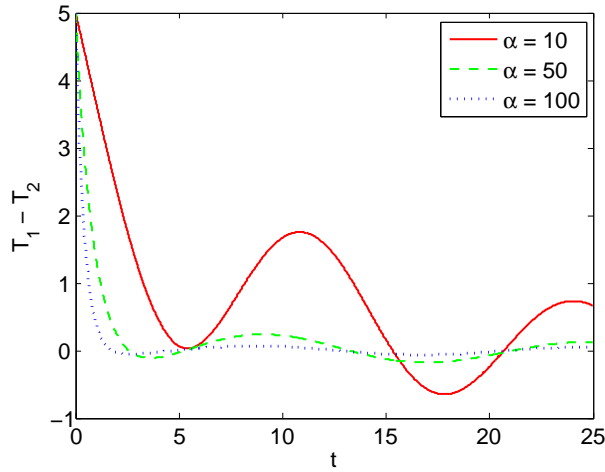


Fig. 3 Thermalization of the thermodynamic oscillators. Because of the exchange of the energy, the two volumes of thermodynamic oscillator which initially have different temperatures will equilibrate to the same one.

Of course, the ratio between the quantum and classical energies is important; however, not only this value defines the evolution. If the energy of the quantum system is greater than kT but the mass of particles of the environment is much larger than the wall, it still plays a role of a heat bath.

4 Results

Fig. 4 shows how different dynamics of the quantum subsystem for the case of different parameters can be. Line 3 shows how quantum system behaves in the case of small β_2 . This situation is similar to the heat bath and we see monotonic decay of the energy of the quantum system. Lines 1 and 2 appear when the mass of volumes is comparable to the mass of the wall between of them. In this case we see oscillations caused by exchange of energy between quantum and classical systems. Lines 1 and 2 reflect different initial temperatures of the volumes. If the temperature of volume coupled to the quantum system is larger than the temperature of the other part we get line 2, otherwise the quantum system evolves according to the line 1.

One can argue how energy of quantum subsystem can be of the same order (or even larger) then the energy of environment. However, “The energy of a single quantum of a CO stretch is 10 times what kT is at room temperature. In effect, shedding a quantum of vibration is equivalent to plunging a red-hot iron into our cold liquid...” [22].

The nonlinear thermodynamic master equation together with the equation which expresses the effect of feedback from quantum system to classical environment describes the whole evolution of the closed quantum-classical system.

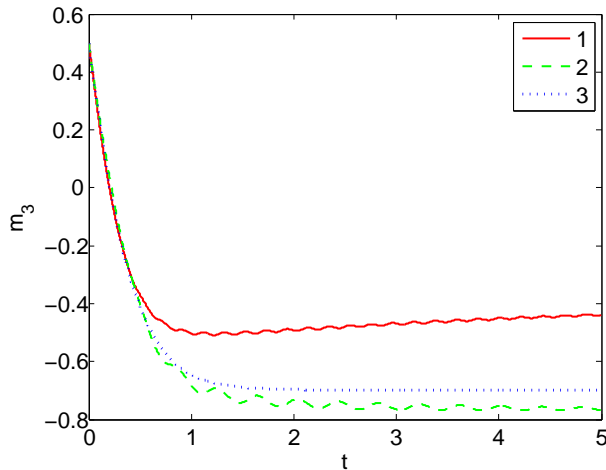


Fig. 4 Energy relaxation of the two-level quantum system coupled to the thermodynamic oscillator. The parameters are: $\omega = 150$, (1) $T_1 = 75$, $T_2 = 250$, $\beta_2 = 1$, (2) $T_1 = 75$, $T_2 = 10$, $\beta_2 = 1$, (3) $T_1 = 75$, $T_2 = 250$, $\beta_2 = 0.0001$.

The quantum system affects the environment a lot, as is shown Fig. 5, and its dynamics is changed not only quantitatively, but also qualitatively. The equilibrium value of the difference of the two temperatures is the same (they are equal), but the dynamics is not the same. An interesting question arises: why the difference between the energies of the two volumes becomes more pronounced without the effect of the feedback. In order to understand this we need Fig. 6. It is clear that the initial value of the energy of the quantum system is much smaller than the classical one which cools the initially colder volume. With the feedback effect the energy of the quantum system flows to the classical system that diminishes the difference of the energies of the volumes.

As it was mentioned before, the nonlinear thermodynamic master equation guarantees the conservation of the energy and positivity of the total entropy production. Figs. 6 and 7 demonstrate this.

5 Conclusions and discussions

As a conclusion, we want to say that we demonstrate the simplest example of interaction between the open quantum system and its classical environment. We show how the interplay between the energies of quantum and classical systems is reflected by the dynamics. The main advantages of the nonlinear thermodynamic master equation (positivity of the entropy production, the conservation of the energy of the total system, and the feedback effect) were shown. Now we want to discuss more interesting applications of the formalism. The most natural practical application of our approach can be an investiga-

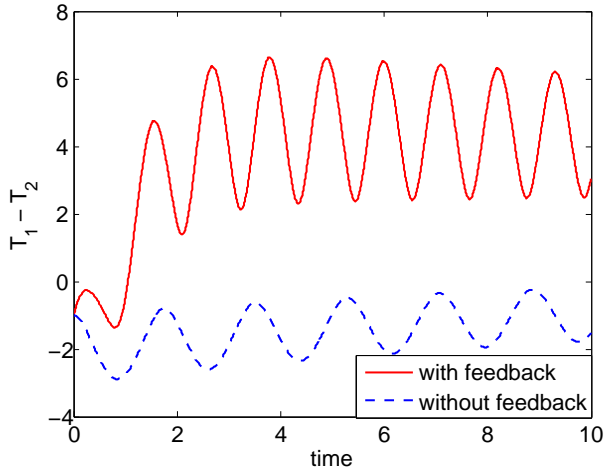


Fig. 5 Effect of the reaction from the quantum system on the thermodynamic oscillator. The parameters are: $\omega = 25$, $T_1 = 3$, $T_2 = 4$, $N = 1$. The equilibrium value of the both temperatures is equal (the difference goes to zero); however, the effect of the feedback changes dynamics seriously.

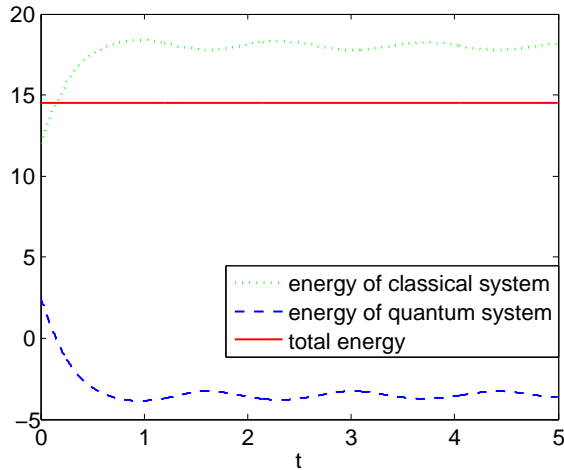


Fig. 6 The conservation of the total energy. The energy of the quantum system and of the environment change in time, but total the energy is constant. The parameters are: $\omega = 25$, $T_1 = 3$, $T_2 = 5$, $N = 1$

tion of *vibrational relaxations in liquids* [23]. In the liquid phase in most cases transitional and rotational degrees of freedom are clearly distinguishable from vibrational ones. Vibrational frequencies are typically larger than the thermal energy which results in a fact that only a few vibrational states are thermally populated. On the other hand, rotational and translational modes have

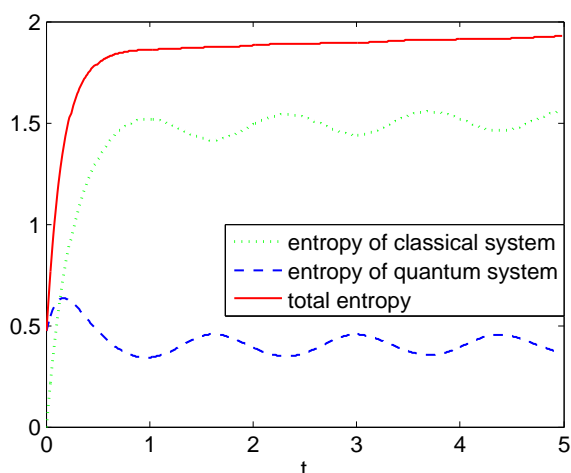


Fig. 7 The entropy of the total system always increases even though the entropy of the quantum and classical system can diminish. The parameters are the same in Fig 6

lower frequencies and more states are thermally populated. As a result, classical physics can be applied to describe their dynamics. Thermodynamics and hydrodynamics are the most suitable tools for this task. In addition, it is important to mention that vibrational phase and energy relaxation times can be as short as a few picoseconds, and may thus be comparable to the relaxation times of environment.

Another application is *electron transfer* [24]. This process is essentially a change in the electronic charge distribution in the molecular systems (solvent). Whereas electronic states are assumed to be a quantum system, the surrounding dielectric environment can be considered to be classical. In the Marcus theory of electron transfer the solvent is taken as a dielectric continuum characterized by a local dielectric function. Methods of classical thermodynamics and electrostatics can be applied to investigate Debye and non-Debye dielectric relaxation of environment (solute). The same description of the environment is valid for *proton transfer* [24].

One more application is a coupling of quantum degrees of freedom to a classical *chaotic system*. During the last decades this approach to study open quantum system has become very popular. According to our formalism, environment can be described with the help of thermodynamics of chaotic systems [25].

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