Quantum Fokker-Planck-Kramers equation and entropy production

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We use a canonical quantization procedure to set up a quantum Fokker-Planck-Kramers equation that accounts for quantum dissipation in a thermal environment. The dissipation term is chosen to ensure that the thermodynamic equilibrium is described by the Gibbs state. An expression for the quantum entropy production that properly describes quantum systems in a nonequilibrium stationary state is also provided. The time-dependent solution is given for a quantum harmonic oscillator in contact with a heat bath. We also obtain the stationary solution for a system of two coupled harmonic oscillators in contact with reservoirs at distinct temperatures, from which we obtain the entropy production and the quantum thermal conductance.

Ordinary Brownian motion and other stochastic phenomena with an underlying motion that follows the laws of classical mechanics are well described by the Fokker-Planck-Kramers (FPK) equation [1–4], which accounts for the classical dissipative behavior in a thermal environment. Quantum dissipation [5], on the other hand, cannot be explained by the classical FPK equation and requires an extension of the stochastic theory to the domain of quantum mechanics. In fact, many approaches to a stochastic theory of quantum systems have been put forward [5–20]. We mention the approach of Lindblad [9], which uses a nonunitary time evolution of the density matrix, and the approach of Caldeira and Leggett [15,16], in which a quantum system interacts with a heat reservoirs composed by a collection of harmonic oscillators. The approach to a stochastic theory of quantum systems that we consider here is based on a quantum version of the classical FPK equation. The construction of the quantum FPK equation that we consider here is based on the canonical quantization of the classical FPK equation. The resulting equation is similar to the one found by Caldeira and Leggett [16], but differs by the dissipation term, which we choose in such a way that in equilibrium the steady state is the Gibbs state.

The classical FPK equation, when extended to a system of many particles, can also be the basis for a stochastic approach to equilibrium and nonequilibrium thermodynamics [21–26]. Here, we also consider a quantum FPK equation for a system with many degrees of freedom, which is appropriate to describe a thermodynamic system in contact with one or several thermal reservoirs, which serves as the basis for a quantum thermodynamics [27,28]. To this end it is necessary to define the rate of entropy production for quantum system [29–31], which is also provided here.

The present approach is applied to two nonequilibrium situations. In the first, we obtain the time-dependent properties of a quantum harmonic oscillator in contact to a heat reservoir. We find the time-dependent density matrix from which we get the entropy production. In the second case, we apply the present approach to get the nonequilibrium steady-state properties of two coupled quantum oscillators in contact with two heat reservoirs at distinct temperatures. We determine the entropy production as well as the heat flux across the system.

We start with the classical FPK equation, which gives the time evolution of the probability density $P(x,p,t)$ related to

the motion of a particle of mass m subject to a potential $V(x)$ and in contact with a heat reservoir at temperature T [1–4],

$$\frac{\partial P}{\partial t} = -\frac{p}{m}\frac{\partial P}{\partial x} + \frac{dV}{dx}\frac{\partial P}{\partial p} + \gamma\frac{\partial(pP)}{\partial p} + \frac{\gamma m}{\beta}\frac{\partial^2 P}{\partial p^2}, \quad (1)$$

where x and p are the position and momentum of the particle, γ is the dissipation parameter, and $\beta = 1/k_B T$. In the stationary state, it is straightforward to show that $P = (1/Z)e^{-\beta\mathcal{H}}$, which means to say that indeed Eq. (1) describes the contact with a heat bath.

Using the definition of the Poisson brackets $\{A,B\} = (\partial A/\partial x)(\partial B/\partial p) - (\partial A/\partial p)(\partial B/\partial x)$, the FPK Eq. (1) can be written in the form

$$\frac{\partial P}{\partial t} = \{\mathcal{H},P\} + \gamma\{x,pP\} + \frac{\gamma m}{\beta}\{x,\{x,P\}\}, \quad (2)$$

where $\mathcal{H} = p^2/2m + V(x)$ is the Hamiltonian of the system.

A canonical quantization [32] of Eq. (2) can be achieved by replacing the Poisson bracket $\{A,B\}$ by $[\hat{A},\hat{B}]/i\hbar$, where $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator between the quantum operators $\hat{A}$ and $\hat{B}$ associated to the quantities A and B, respectively. For instance, the commutator between x and p is $[x,p] = i\hbar$. This procedure combined with the use of a symmetrized product leads us to the following equation [16]:

$$i\hbar\frac{\partial\rho}{\partial t} = [\mathcal{H},\rho] + \frac{\gamma}{2}[x,\rho p + p\rho] + \frac{\gamma m}{i\hbar\beta}[x,(x,\rho)], \quad (3)$$

where ρ is the density matrix and $\mathcal{H} = p^2/2m + V(x)$ is the quantum Hamiltonian. This procedure will guarantee that, in the classical limit, Eq. (3) will become the FPK Eq. (2). However, as can be verified by a direct substitution, $e^{-\beta\mathcal{H}}$ is not the stationary solution of Eq. (3), except for a free particle.

This simple procedure of replacing the classical Poisson bracket by the quantum commutator and the classical variables by quantum operators does not give an unambiguous prescription to construct a quantum version of a classical equation. Bearing this in mind, we look for a more general quantum version of Eq. (2) by assuming the following form for the quantum FPK equation:

$$i\hbar\frac{\partial\rho}{\partial t} = [\mathcal{H},\rho] + \frac{\gamma}{2}[x,\rho g + g^\dagger\rho] + \frac{\gamma m}{i\hbar\beta}[x,(x,\rho)], \quad (4)$$

where the operator g does not depend on ρ and are to be found based on two assumptions. First, $g \to p$ in the classical limit, so that Eq. (4) goes onto Eq. (2) in this limit. Second, we require that $\rho_0 = (1/Z)e^{-\beta \mathcal{H}}$ is the stationary solution of Eq. (4) for any potential V. To this end, we begin by writing Eq. (4) in the form

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] - [x, J(\rho)], \tag{5}$$

where

$$J(\rho) = -\frac{\gamma}{2}(\rho g + g^\dagger \rho) - \frac{\gamma\, m}{i\hbar\beta}[x, \rho]. \tag{6}$$

In the stationary state, which is understood here as the thermodynamic equilibrium state, $J = 0$, that is, the insertion of the equilibrium density matrix $\rho_0 = (1/Z_0)e^{-\beta\mathcal{H}}$ into Eq. (6) should result in $J(\rho_0) = 0$. This yields

$$g = -\frac{m}{i\hbar\beta}\left(\rho_0^{-1}x\rho_0 - x\right) = -\frac{m}{i\hbar\beta}(e^{\beta\mathcal{H}}xe^{-\beta\mathcal{H}} - x), \tag{7}$$

which is the desired expression for g. The expansion of the first term between parentheses in powers of β allows us to write g in a form involving nested commutators,

$$g = p + \frac{\beta}{2!}[\mathcal{H}, p] + \frac{\beta^2}{3!}[\mathcal{H}, (\mathcal{H}, p)] + \frac{\beta^3}{4!}\{\mathcal{H}, [\mathcal{H}, (\mathcal{H}, p)]\} + \cdots \tag{8}$$

In the classical limit, all terms, except the first, on the right-hand side of Eq. (8) vanish and g approaches p as desired.

Next we wish to connect the present approach with nonequilibrium thermodynamics. To this end we consider the evolution of the free energy F, defined by $F = U - TS$, where $U = \langle \mathcal{H} \rangle$ and S is the von Neumann entropy, $S = -k_B \text{Tr}\{\rho \ln \rho\}$. The expression for the free energy can be written in the form

$$F = k_B T \, \text{Tr}\{\rho \ln \rho - \rho \ln \rho_0\} + F_0, \tag{9}$$

where $\rho_0 = (1/Z)e^{-\beta\mathcal{H}}$ is the equilibrium density matrix and $F_0 = -k_B T \ln Z_0$. Using Klein's inequality [33], $\text{Tr}\{\rho \ln \rho - \rho \ln \rho_0\} \geqslant 0$, it follows at once that $F \geqslant F_0$.

The time derivative of F is related to the entropy production rate Π by $dF/dt = -T\Pi$ [23,26]. Using Eq. (5) to calculate dF/dt from Eq. (9), we arrive at the following expression for the rate of entropy production:

$$\Pi = \frac{k_B}{i\hbar}\text{Tr}\{[x, J(\rho)](\ln \rho - \ln \rho_0)\}, \tag{10}$$

which can also be written as

$$\Pi = \frac{k_B}{i\hbar}\text{Tr}\{[x, J(\rho)](\ln \rho + \beta\mathcal{H}\}. \tag{11}$$

It is worth mentioning that, in the classical limit, the entropy production rate reduces to the following expression [23,26]:

$$\Pi = \frac{1}{\gamma\,Tm}\int \frac{J^2}{P}dxdp, \tag{12}$$

which is a quantity manifestly nonnegative, where $J = -\gamma pP - (\gamma m/\beta)\partial P/\partial p$.

Let us determine g for some simple situations. In the case of a free particle, for which $\mathcal{H} = p^2/2m$, the quantity g simplifies substantially. In this case all the commutators in Eq. (8) vanish

and $g = p$. The resulting quantum FPK equation reduces to Eq. (3), which is thus understood as the equation describing a quantum Brownian motion of a free particle.

In the case of an harmonic oscillator, for which $\mathcal{H} = p^2/2m + m\omega^2 x^2/2$, a straightforward calculation gives $g = ap + ibx$, where a and b are real numbers, given by

$$a = \frac{1}{\beta\hbar\omega}\sinh\beta\hbar\omega, \qquad b = \frac{m}{\beta\hbar}(\cosh\beta\hbar\omega - 1). \tag{13}$$

The time evolution of the covariances are

$$\frac{d}{dt}\langle p^2 \rangle = -m\omega^2(\langle px \rangle + \langle xp \rangle) + \hbar b\gamma - 2a\gamma\langle p^2 \rangle + \frac{2\gamma m}{\beta}, \tag{14}$$

$$\frac{d}{dt}\langle x^2 \rangle = \frac{1}{m}(\langle px \rangle + \langle xp \rangle), \tag{15}$$

$$\frac{d}{dt}\langle px \rangle = \frac{d}{dt}\langle xp \rangle = \frac{1}{m}\langle p^2 \rangle - m\omega^2\langle x^2 \rangle$$
$$- \frac{a\gamma}{2}(\langle px \rangle + \langle xp \rangle). \tag{16}$$

At the stationary state, $\langle xp \rangle = -\langle xp \rangle = i\hbar/2$, $\langle p^2 \rangle = (\hbar b/2a) + (m/a\beta)$, and $\langle x^2 \rangle = \langle p^2 \rangle/m\omega^2$. From these results one gets the expected expression for $\langle \mathcal{H} \rangle$,

$$\langle \mathcal{H} \rangle = \hbar\omega\left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right). \tag{17}$$

A time-dependent solution of the quantum FPK equation for the harmonic oscillator is

$$\rho = \frac{1}{Z}\exp\left\{-\frac{c_1}{2}p^2 - \frac{c_2}{2}x^2 - \frac{c_3}{2}(xp + px)\right\}, \tag{18}$$

where c_1, c_2, and c_3 are time-dependent parameters. That this form is indeed a solution can be verified by replacing Eq. (18) into the FPK equation. From Eq. (18) one obtains the relation between the covariances $\langle p^2 \rangle$, $\langle x^2 \rangle$, $\langle xp + px \rangle$ and the parameters c_1, c_2, c_3 so that from the time-dependent solution of Eqs. (14), (15), and (16), we may find the time behavior of c_1, c_2, c_3, and ρ. We are thus able to get the time-dependent properties of the harmonic oscillator in contact with a heat reservoir, given an initial condition. Using this procedure, we have determined the time behavior of several quantities, including the free energy F and the production of entropy Π, which are shown in Fig. 1. In this figure we used initial conditions such that $\langle p^2 \rangle/m\hbar\omega = 1/2$, $m\langle x^2 \rangle/\hbar\omega = 1/2$, and $\langle xp + px \rangle = 0$.

As stated before, the present approach may serve as the basis for a nonequilibrium thermodynamics. The fundamental properties that distinguish nonequilibrium from equilibrium are the production of entropy, whose nonnegativity is equivalent to the second law, and the existence of fluxes such as heat flow. It is convenient to distinguish two forms of nonequilibrium. A system may be out of equilibrium because it did not yet reach equilibrium. This was exemplified by the case of an harmonic oscillator that we have just considered. As shown in Fig. 1, the entropy production is nonnegative but vanishes for large times because the system reaches equilibrium. Another aspect is the nonequilibrium behavior in systems that are in the steady state, as happens to a system in contact to two heat reservoirs
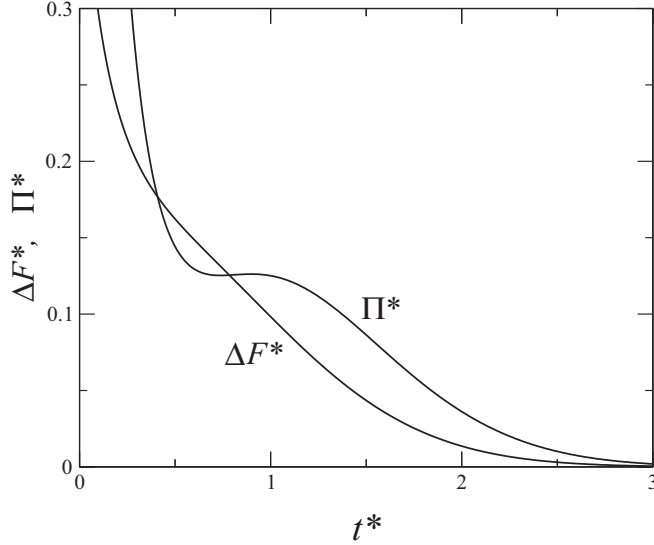
FIG. 1. Free energy and rate of entropy production as functions of time for a quantum oscillator in contact with a heat reservoir. The dimensionless quantities in the plot are as follows: $\Delta F^* = (F - F_0)/\hbar\omega$, $\Pi^* = \Pi/k_B\omega$, and $t^* = \omega t$. The values of the parameters are $k_B T/\hbar\omega = 1$ and $\gamma/\omega = 1$.

at distinct temperatures. In this case, there will be a permanent heat flow and the production of entropy is positive and constant in time. To deal with this case we consider next a system of many interacting particles in contact with heat reservoirs at distinct temperatures.

A system of interacting particles is described by the Hamiltonian

$$\mathcal{H} = \sum_i \frac{p_i^2}{2m} + V(x), \quad (19)$$

where here x represents the collection of the positions $\{x_i\}$ of the particles and p_i is the momentum conjugate to x_i. The quantum FPK equation for this case reads

$$i\hbar \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] - \sum_i [x_i, J_i(\rho)], \quad (20)$$

where $\rho(x, v)$ is the density matrix and

$$J_i(\rho) = -\frac{\gamma_i}{2}(\rho g_i + g_i^\dagger \rho) - \frac{\gamma_i m}{i\hbar\beta_i}[x_i, \rho], \quad (21)$$

with

$$g_i = -\frac{m}{i\hbar\beta_i}(e^{\beta_i \mathcal{H}} x_i e^{-\beta_i \mathcal{H}} - x_i). \quad (22)$$

We are considering a general case in which each particle is in contact with a heat reservoir at a temperature T_i and $\beta_i = 1/k_B T_i$.

Let us assume that some particles are in contact ($\gamma_i \neq 0$) with the same reservoir at temperature T, whereas the others are not connected ($\gamma_i = 0$) to any reservoir. In this case, the steady-state solution of the quantum FPK Eq. (20) is the canonical Gibbs density matrix $\rho_0 = (1/Z)e^{-\beta\mathcal{H}}$ because $J_i(\rho_0) = 0$ for each i, a condition that may be understood as detailed balance, and the system is found to be in

thermodynamic equilibrium. It is worth mentioning that the canonical density matrix ρ_0 will be the steady-state solution no matter how many particles are in contact ($\gamma_i \neq 0$) with the reservoirs, as long as there is at least one. This feature distinguishes the present approach from that in which local Lindblad forms are used to describe the contact with heat reservoirs, which does not lead to a thermalization of the system into the Gibbs state [34].

If the temperatures of the heat reservoirs are different from each other then, in the steady state, the system will not be in thermodynamic equilibrium. This nonequilibrium steady state may be characterized by a nonzero production of entropy. In analogy with Eq. (11), we define the rate of entropy production as

$$\Pi = \frac{k_B}{i\hbar} \sum_i \text{Tr}\{[x_i, J_i(\rho)](\ln \rho + \beta_i \mathcal{H})\}. \quad (23)$$

The time variation of the von Neumann entropy $S = -k_B \text{Tr}\{\rho \ln \rho\}$ can be written as

$$\frac{dS}{dt} = \frac{k_B}{i\hbar} \sum_i \text{Tr}\{[x_i, J_i(\rho)] \ln \rho\}, \quad (24)$$

so that the flux of entropy, $\Phi = \Pi - dS/dt$, from the system toward the reservoirs is thus

$$\Phi = \frac{1}{i\hbar} \sum_i \frac{1}{T_i} \text{Tr}\{[x_i, J_i(\rho)]\mathcal{H}\}. \quad (25)$$

From the quantum FPK Eq. (20), the evolution of the average of the energy $U = \langle \mathcal{H} \rangle$ is given by

$$\frac{dU}{dt} = -\sum_i \phi_i, \quad (26)$$

where

$$\phi_i = \frac{1}{i\hbar} \text{Tr}\{[x_i, J_i]\mathcal{H}\} \quad (27)$$

is the heat flux from the system toward the reservoir at temperature T_i, so that we may write

$$\Phi = \sum_i \frac{\phi_i}{T_i}. \quad (28)$$

Replacing J_i in the expression for ϕ_i, we get

$$\phi_i = \gamma_i \left(\frac{1}{2m} \langle g_i p_i + p_i g_i^\dagger \rangle - k_B T_i \right). \quad (29)$$

For two reservoirs in the stationary state, $\phi_1 + \phi_2 = 0$ and

$$\Phi = \frac{\phi_1}{T_1} + \frac{\phi_2}{T_2} = \phi \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (30)$$

where $\phi = \phi_2 = -\phi_1$ is interpreted as the heat flow across the system from reservoir 1 to reservoir 2.

Let us consider a system of two coupled harmonic oscillators, described by the Hamiltonian

$$\mathcal{H} = \frac{1}{2m}(p_1^2 + p_2^2) + \frac{k}{2}(x_1 - x_2)^2 + \frac{k'}{2}(x_1^2 + x_2^2), \quad (31)$$

in contact with reservoirs at temperature T_1 and T_2. In this case, the quantities g_1 and g_2 are given by

$$g_i = \sum_{j=1,2} (a_{ij} p_j + i b_{ij} x_j), \tag{32}$$

where

$$a_{ij} = \frac{\sinh(\beta_i \hbar \omega)}{2\beta_i \hbar \omega} \pm \frac{\sinh(\beta_i \hbar \omega')}{2\beta_i \hbar \omega'}, \tag{33}$$

$$b_{ij} = \frac{m \cosh(\beta_i \hbar \omega) - 1}{2\beta_i \hbar} \pm \frac{m \cosh(\beta_i \hbar \omega') - 1}{2\beta_i \hbar}, \tag{34}$$

where the plus and minus signs are to be used when $i = j$ and $i \neq j$, respectively, and $\omega = \sqrt{k'/m}$ and $\omega' = \sqrt{(2k+k')/m}$.

From the quantum FPK Eq. (20), and using g_i given by Eq. (32), we set up the evolution equations for the correlations $\langle x_i x_j \rangle$, $\langle x_i p_j \rangle$, and $\langle p_i p_j \rangle$. From the solution of these equations we can determine the heat flow ϕ, given by Eq. (29). In the stationary state, we find

$$\phi = \frac{k^2}{k'm\gamma(a_1 + a_2)} \left(\frac{\hbar\omega}{e^{\beta_1 \hbar\omega} - 1} - \frac{\hbar\omega}{e^{\beta_2 \hbar\omega} - 1} \right), \tag{35}$$

valid for $k \ll k'$, where

$$a_1 = \frac{\sinh(\beta_1 \hbar\omega)}{\beta_1 \hbar\omega}, \qquad a_2 = \frac{\sinh(\beta_2 \hbar\omega)}{\beta_2 \hbar\omega}. \tag{36}$$

We have used the same dissipation parameters, $\gamma_1 = \gamma_2 = \gamma$. The heat flux ϕ, given by Eq. (35), is positive if $T_2 > T_1$ and negative if $T_2 < T_1$. Therefore, the entropy production Π,

which in the stationary state is identified as the entropy flux Φ, given by Eq. (30), is nonnegative, as desired. Notice that, in the classical limit, Eq. (35) reduces to the expression that one obtains from the classical FPK equation [23,35].

The quantum thermal conductance κ is obtained by writing $T_{1,2} = T \pm \Delta T/2$ and $\phi = \kappa \Delta T$. For small values of ΔT,

$$\kappa = \frac{k_B k^2}{2k'm\gamma a} \left(\frac{\beta \hbar\omega}{e^{\beta\hbar\omega} - 1} \right)^2, \tag{37}$$

where a is given by Eq. (13).

In summary, by the use of a canonical quantization we have set up a quantum FPK equation describing the time evolution of quantum systems in contact with heat reservoirs. For a system in contact with just one heat reservoir the stationary state is the equilibrium Gibbs state. We have applied the present approach to a system of two coupled harmonic oscillators in contact with reservoirs at distinct temperatures. From the steady-state solution of the quantum FPK equation we have obtained the heat flux and the entropy production, which was shown to be positive.

As a final comment, it should be pointed out that the results we have obtained for the harmonic oscillator in equilibrium do not depend on damping parameter. Since this is to be expected when the damping parameter is small [5], it follows that the present approach is able to give the expected results in the quantum regime at least in the low damping regime.

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