On the microscopic basis of Newton’s law of cooling and beyond

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Abstract

The microscopic basis of Newton’s law of cooling and its modification when the difference in temperature between the system and the surroundings is very large is discussed. When the system of interest is interacting with a small bath, the effect of the dynamical evolution of the bath variables is important to find out its dynamical feedback on the system. As in the usual system-bath approach, however, the bath is finally considered to be in thermal equilibrium and thereby provides an effective generalization of the Born-Markov master equation. It is shown that the cooling at early time is faster than that predicted by Newton’s law due to the dynamical feedback of the bath.

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I. Introduction

Classically the phenomenon of cooling of a bulk body may be considered as a process where the flow of heat from the hotter body to a colder environment is governed by the Newton’s law of cooling, namely,

$$-\frac{dT(t)}{dt} = \gamma(T(t) - T_R),$$

with $T(t)$ be the instantaneous temperature of the body, $T_R$ be the temperature of the environment and $\gamma$ be the characteristic decay constant, respectively. The solution of Eq.(1) reads

$$T(t) = T_0e^{-\gamma t} + T_R(1 - e^{-\gamma t}),$$

where $T_0$ is the initial temperature of the body at $t = 0$ such that $T_R < T_0$. The classical rate equation does not contain any non-linear term and it is valid if the difference between the temperature of the system and environment is small.

On the other hand, the cooling of the neutral atoms is generally performed by various coherent laser-cooling techniques, which primarily concern with the reduction of the kinetic motion of the center-of-mass of the trapped atoms [1,2]. However, if we consider the coherent cooling of the molecules [3], then the contribution to the thermal energy arises not only from the motion of their centre of mass, but also from their rotational or vibrational motion. Thus for an ensemble of trapped molecules the cooling requires the ceasing of the momentum associated with all possible degrees of freedom, although a priori it is difficult to ascertain which of the degree of freedom contributes most significantly. If we neglect the translational and rotational motion of the trapped molecules, the dissipation of temperature associated with the vibrational degrees of freedom may be formulated quantitatively within the framework of the standard dissipation theory of the damped harmonic oscillator. To formulate the theoretical basis of the vibrational cooling, we assume that a molecule with one or few modes of vibration as our system of interest which dissipates its energy into the large number of other modes acting effectively acts
as the reservoir. In the density matrix formalism of the system-reservoir composite model, the nontrivial weak coupling between the system with the reservoir effectively induces a damping in the system. Consequently, we obtain the Born-Markov master equation of the reduced density matrix $\rho$, where the reservoir oscillators are completely eliminated in terms of the system variables \[4,5\] as

$$\frac{d\rho}{dt} = -i\omega_0[a^\dagger a, \rho] - \gamma(1 + \bar{n}_R(T_R))[a^\dagger a\rho - 2a\rho a^\dagger + \rho a^\dagger a] - \gamma\bar{n}_R(T_R)(aa^\dagger\rho - 2a^\dagger\rho a + \rho aa^\dagger), \quad (3)$$

where the frequency of the system oscillator is $\omega_0$ with $[a, a^\dagger] = 1$ and the average thermal excitation number of the bath is $\bar{n}_R(T_R) = \frac{1}{e^{\frac{\hbar \omega_0}{kT_R}} - 1}$, where $T_R$ is the temperature of the reservoir. Thus, it follows from the master equation that the time evolution of average photon number of the system mode, $\frac{d\bar{n}_S(t)}{dt} = Tr[a^\dagger a\frac{d\rho}{dt}]$, with frequency $\omega_0$ is described by the rate equation

$$-\frac{d\bar{n}_S(t)}{dt} = \gamma(\bar{n}_S(t) - \bar{n}_R(T_R)), \quad (4)$$

and its solution is given by

$$\bar{n}_S(t) = \bar{n}_R(T_R) + (\bar{n}_S(0) - \bar{n}_R(T_R))e^{-\gamma t}. \quad (5)$$

Thus, the vibrational cooling corresponds to the feeding of the thermal photon from the system to the reservoir until the system photon number equilibrates with that of the reservoir. This process is known as the thermalization and it is evident from Eq.(5) that, similar to the classical cooling, it occurs after an infinitely large time, namely, $\bar{n}_S(\infty) = \bar{n}_R(T_R)$. We can associate the instantaneous average photon number of the system mode with an effective temperature $T(t)$ by using the relation

$$\bar{n}_S(T(t)) = \frac{1}{e^{\frac{\hbar \omega_0}{kT(t)}} - 1}, \quad (6)$$

which in the high temperature limit gives, $\bar{n}_S(T(t)) \approx \frac{kT(t)}{\hbar \omega_0}$. In the same limit, the initial system photon number and the reservoir photon number are given by $\bar{n}_S(T_0) \approx \frac{kT_0}{\hbar \omega_0}$ and $\bar{n}_R(T_R) \approx \frac{kT_R}{\hbar \omega_0}$.
respectively; putting these values in Eq.(5) we recover Eq.(2). Therefore, the classical Newton’s cooling law in Eqs.(1) and (2) can be obtained from the high temperature limiting situation of the Born-Markov master equation in Eqs.(3) and (5). This is valid when the difference in average energy per mode between the system and the reservoir is small, whereby the reservoir does not change with time due to the acceptance of energy from the system of interest.

In the crossroad of various approaches and applications of the system-reservoir composite formalism, the necessity of the finite bandwidth of the reservoir [6-12] was envisaged right from the beginning which leads to the possible modification of Eq.(3). The recent experiments involving ultra-fast time scale [13-15], correlated emission laser (CEL) pulse with adjustable memory time [16], experiments on cavity electrodynamics [17] etc, have significant impact in the understanding of the models beyond the Born-Markov approximation. However, in all previous studies, the assumption that works at more subtle level is that the photon absorbed by the reservoir from the system cannot bring any dynamical change with it because of the small difference of the energy between the system and average energy of each degree of freedom of the reservoir. It is therefore of natural interest how the situation changes if we consider that the energy of the system is large enough in comparison to that of each mode of the reservoir. In this paper we shall show that, due to the large difference of average energy between the system and each reservoir mode, the flow of the thermal photon of substantial energy from the system to the reservoir effectively leads to the dynamical evolution of the reservoir. Our primary objective is to discuss the vibrational cooling of a system with large energy content by incorporating the aforesaid dynamical evolution of the reservoir.

The remaining sections of the paper are organized as follows. In Sec. II we have developed a formalism to incorporate the evolution of the reservoir and show how it effectively generalizes the Born-Markov master equation beyond leading order of the decay constant. We apply our formalism to the damped harmonic oscillator in Sec. III and show that how it affects the thermalization time to make it short. We conclude by highlighting the essence of the paper and discussing its outlook.
II. Formalism

The Hamiltonian of a system interacting with the reservoir is given by

$$H = H_S + H_R + V \equiv H_0 + V,$$

where $H_S$, $H_R$ represent the Hamiltonians of the system and reservoir, respectively and $V$ is the interaction between them. Let $\kappa(t)$ be the joint density matrix of the composite system in the Interaction Picture (IP); the corresponding evolution equation is

$$\frac{\partial \kappa(t)}{\partial t} = -\frac{i}{\hbar} [V(t), \kappa(t)].$$

The solution of the equation is given by

$$\kappa(t) = \kappa(0) - \frac{i}{\hbar} \int_0^t dt'[V(t'), \kappa(0)] + \left(\frac{e^{-iH_0}}{\hbar}\right)^2 \int_0^t dt' \int_0^t dt'' [V(t'), [V(t''), \kappa(t'')]].$$

We consider the interaction Hamiltonian in the IP is of the following form:

$$V(t) = \hbar \sum_i Q_i(t) F_i(t),$$

where $Q_i(t)$ and $F_i(t)$ be the system and reservoir operators, respectively, in IP. Using the factorization ansatz, namely, $\kappa(0) \approx s(0) f(0)$ and $\kappa(t') \approx s(t') f(t'')$, respectively, and by noting the fact that $Tr_R \kappa(t) = s(t)$, the trace over the reservoir mode in Eq.(9) yields

$$s(t) = s(0) - i \int_0^t dt' \sum_i \langle F_i(t') \rangle_R [Q_i(t'), s(0)] -$$

$$\int_0^t dt' \int_0^t dt'' \sum_{i,j} \{ Tr_R[F_i(t') F_j(t'') f(t'')][Q_i(t') Q_j(t'') s(t'') - Q_j(t'') s(t'') Q_i(t')] -$$

$$Tr_R[F_j(t'') F_i(t') f(t'')][Q_i(t') s(t'') Q_j(t'') - s(t'') Q_j(t'') Q_i(t')]\},$$

where $\langle \ldots \rangle_R = Tr_R[\ldots f(0)]$ is the average of the reservoir operators. Taking the derivative of Eq.(11) with respect to $t'$ we obtain (we redefine $t''$ by $t'$ and $t'$ by $t$),

$$\frac{\partial s(t)}{\partial t} = -\sum_{i,j} \int_0^t dt' \{ [Q_i Q_j s(t') - Q_j s(t') Q_i] Tr_R[F_i(t) F_j(t') f(t')] -$$

$$[Q_i s(t') Q_j - s(t') Q_j Q_i] Tr_R[F_j(t') F_i(t) f(t')]\} \exp[i(\omega_i t + \omega_j t')],$$

where $\omega_i$ and $\omega_j$ are the frequencies of the reservoir modes.
where $\omega_i^S$ be the characteristic frequencies of the system and the term linear in reservoir operator vanishes by the symmetry argument. The system oscillator in the IP in $V(t)$ can be expressed in the Schrodinger picture (SP) by using the standard prescription,

$$Q_i(t) = e^{i\hbar H_S t} Q_i e^{-i\hbar (H_S)t} = Q_i e^{-i\omega_i^S t}. \quad (13)$$

Now, replacing $t'$ by $t - \tau$ in Eq.(12) and assuming the Born-Markov approximation [4], namely, $s(t - \tau) \approx s(t)$ for large $t$, the generalized master equation of the reduced density operator in Schrodinger picture, $S$, is obtained as

$$\frac{dS}{dt} = -i \frac{\hbar}{\hbar} [H_S, S] - \sum_{i,j} \{ [Q_i Q_j S - Q_j SQ_i] W_{ij}^+[t] - [Q_i SQ_j - SQ_j Q_i] W_{ji}^-[t] \} \delta (\omega_i^S + \omega_j^S), \quad (14)$$

where

$$W_{ij}^+[t] = \int_0^t d\tau e^{i\omega_i^S \tau} Tr_R [F_i(t) F_j(t - \tau) f(t - \tau)], \quad (15a)$$

$$W_{ji}^-[t] = \int_0^t d\tau e^{i\omega_j^S \tau} Tr_R [F_j(t - \tau) F_i(t) f(t - \tau)], \quad (15b)$$

which are to be calculated in different situations.

To include the evolution of the reservoir in this scenario, using $Tr_{SK}(t) = f(t)$ along with Eq.(10), the trace of Eq.(9) over the system yields

$$f(t - \tau) = f(0) - i \sum_k \int_0^{t-\tau} dt_1 \langle Q_k(t_1) \rangle_S [F_k(t_1), f(0)] -$$

$$\sum_{i,m} \int_0^{t-\tau} dt_1 \int_0^{t_1} dt_2 \langle F_i(t_1) F_m(t_2) f(0) - F_m(t_2) f(0) F_i(t_1) \rangle \langle Q_i(t_1) Q_m(t_2) \rangle_S -$$

$$(F_i(t_1) f(0) F_m(t_2) - f(0) F_m(t_2) F_i(t_1)) \langle Q_m(t_2) Q_i(t_1) \rangle_S + ..., \quad (16)$$

where $\langle ... \rangle_S = Tr_S[... s(0)]$ represents the average of the system operator which depends on the initial population distribution of the system. In deriving Eq.(16), unlike previous case, we use the ansatz $\kappa(t') \approx \kappa(0)$ to terminate the series beyond the second order in interaction [4]. Plucking Eq.(16) back into Eq.(15a), we find
\[ W_{ij}^+[t] = W_{ij}^{+0}[t] + \hat{W}_{ij}^+[t] + ..., \] (17)

where \( W_{ij}^{+0}[t] = \int_0^t d\tau e^{i\omega_{ij}\tau} \langle F_i(t)F_j(t-\tau) \rangle_R \) is the usual lowest order reservoir correlator [4,5]. In Eq.(17) the term next to lowest order arises due to the correlation among the system oscillators, and it is given by

\[
\hat{W}_{ij}^+[t] = -i \sum_l \int_0^t \int_0^\tau d\tau_1 \langle Q_l(t_1) \rangle_S \left\{ \langle F_i(t)F_j(t-\tau)F_k(t_1) \rangle_R - \langle F_k(t_1)F_i(t)F_j(t-\tau) \rangle_R \right\} - \\
\sum_{l,m} \int_0^t \int_0^\tau d\tau_1 \int_0^{t_1} dt_2 \\bigg[ \langle F_l(t_1)F_i(t)F_j(t-\tau)F_m(t_2) \rangle_R - \langle F_m(t_2)F_i(t)F_j(t-\tau)F_l(t_1) \rangle_R \langle Q_m(t_2)Q_l(t_1) \rangle_S \bigg]. \] (18)

It is customary to write the reservoir Hamiltonian in the following form:

\[ H_R = \sum_k \hbar \omega_k (b_k^\dagger b_k + \frac{1}{2}), \] (19)

where \( \omega_k \) is the frequency of the reservoir modes. The time-dependent reservoir operator in the IP appearing in Eq.(18) can be expressed in the SP as

\[ F_1(t) = \sum_p \kappa_p e^{i(\hbar/\hbar)t} b_p e^{(-i/\hbar)H_R t} = \sum_p \kappa_p b_p e^{-i\omega_p t}, \] (20a)

\[ F_2(t) = \sum_q \kappa_q e^{i(\hbar/\hbar)t} b_q^\dagger e^{(-i/\hbar)H_R t} = \sum_q \kappa_q b_q^\dagger e^{i\omega_q t}, \] (20b)

where \( \omega_l \) (\( l = p, q \)) is the angular frequency of the reservoir oscillators mode and \( \kappa_l \) the coupling constants, respectively. From Eq.(18) we now proceed to evaluate the spectral density function \( \hat{W}_{12}^+[t] \) for \( i = 1 \) and \( j = 2 \),

\[
\hat{W}_{12}^+[t] = -\sum_{l,m} \int_0^t \int_0^\tau d\tau_1 \int_0^{t_1} dt_2
\]
\[
\left[ \langle F_1(t)F_2(t-\tau)F_1(t_1)F_m(t_2)\rangle_R - \langle F_1(t_1)F_1(t)F_2(t-\tau)F_m(t_2)\rangle_R \right] \langle Q_l(t_1)Q_m(t_2)\rangle_S + \\
\left[ \langle F_m(t_2)F_1(t_1)F_2(t-\tau)\rangle_R - \langle F_m(t_2)F_1(t)F_2(t-\tau)F_1(t_1)\rangle_R \right] \langle Q_m(t_2)Q_l(t_1)\rangle_S, \tag{21}
\]

where, once again, the term linear in the system operators is dropped by the symmetry argument. Throughout the treatment we assume that the reservoir is in a thermal distribution and thus only the diagonal terms will survive. Substituting Eqs. (13), (20a) and (20b) in Eq. (21), we obtain (for details, see Appendix)

\[
\hat{W}_{12}^+[t] = \sum_{\tau,s} |\kappa_r|^2 |\kappa_s|^2 e^{i(\omega_r - \omega_s)t} \int_0^t d\tau e^{i(\omega_0 - \omega_r)\tau} \int_0^{t-\tau} dt_1 e^{i(\omega_0 - \omega_s)t_1}
\]

\[
\int_0^{t_1} dt_2 e^{i(\omega_s - \omega_0)t_2} ((2 + \bar{n}_R(\omega_r) + \bar{n}_R(\omega_s, T_R)) \langle Q_1 Q_2 \rangle_S - (\bar{n}_R(\omega_r, T_R) + \bar{n}_R(\omega_s, T_R)) \langle Q_2 Q_1 \rangle_S), \tag{22}
\]

where \(\bar{n}_R(\omega_s, T_R)\) is the average thermal photon number of the reservoir and we have considered the system frequency to be \(\omega_1^S = -\omega_2^S = \omega_0\) for convenience without losing generality. Thus we note that in Eq. (22), the evolution of the reservoir arises due to the correlation functions of the system operators. Finally converting the sum over modes into the frequency space integrals, we find

\[
\hat{W}_{12}^+[t] = \int_0^\infty d\omega_r D(\omega_r) |\kappa(\omega_r)|^2 \int_0^\infty d\omega_s D(\omega_s) |\kappa(\omega_s)|^2 e^{i(\omega_r - \omega_s)t} \int_0^t d\tau e^{i(\omega_0 - \omega_r)\tau}
\]

\[
\int_0^{t-\tau} dt_1 e^{i(\omega_0 - \omega_s)t_1} \int_0^{t_1} dt_2 e^{i(\omega_s - \omega_0)t_2} ((2 + \bar{n}_R(\omega_r, T_R) + \bar{n}_R(\omega_s, T_R)) \langle Q_1 Q_2 \rangle_S - \\
(\bar{n}_R(\omega_r, T_R) + \bar{n}_R(\omega_s, T_R)) \langle Q_2 Q_1 \rangle_S), \tag{23}
\]

where \(D(\omega_r)\) and \(D(\omega_s)\) be the density of states respectively. Proceeding in the similar way we can show that \(\hat{W}_{12}^-[t] = \hat{W}_{21}^-[t]\). The time development of the reservoir for any simple system may be calculated from Eq. (23).
III. Application to simple harmonic oscillator

The vibrational cooling may be modeled by a harmonic oscillator interacting with large number of the reservoir modes resulting damping. The free Hamiltonian and interaction term of such composite system are given by

\[ H_S = \hbar \omega_0 (a^\dagger a + \frac{1}{2}) \]  
\[ V = \hbar \sum_k (\kappa_k a^\dagger b_k + \kappa^*_k a b_k^\dagger), \]

(24a) (24b)

respectively, with the generic reservoir Hamiltonian given by Eq.(19). In Eqs.(24a) and (24b), the system operators are in the Schrödinger picture i.e, \( Q_1 = a^\dagger \) and \( Q_2 = a \). Taking \( \bar{n}_S(t) = \langle a^\dagger a(t) \rangle_S \) to be the average photon number of the system in time \( t \) and the upper limits of integration as \( t, t - \tau, t_1 \to \infty \), Eq.(23) becomes

\[ \hat{W}_{12}[t] = 2\pi^2 D^2(\omega_0) |\kappa(\omega_0)|^4 (\bar{n}_S(t) - \bar{n}_R(T_R))t, \]

(25)

the difference between the instantaneous average excitation number of the system and the thermal average photon number of the reservoir. In deriving Eq.(25) we have neglected the principal parts which correspond to a small Lamb shift. Substituting Eq.(25) in Eq.(17) (with \( i = 1 \) and \( j = 2 \)) and plucking back the resulting equation in Eqs.(15a) and (15b), we obtain a generalized Born-Markov master equation of the damped harmonic oscillator,

\[ \frac{dS}{dt} = -\frac{i}{\hbar}[H_S, S] - \frac{\gamma_1(t)}{2}[a^\dagger a S - 2a S a^\dagger + S a^\dagger a] - \frac{\gamma_2(t)}{2}[a a^\dagger S - 2 a^\dagger S a + S a a^\dagger], \]

(26)

where

\[ \gamma_1(t) = \gamma(1 + \bar{n}_R(T_R)) + \gamma^2(\bar{n}_S(t) - \bar{n}_R(T_R))t, \]  
\[ \gamma_2(t) = \gamma \bar{n}_R(T_R) + \gamma^2(\bar{n}_S(t) - \bar{n}_R(T_R))t, \]

(27a) (27b)

with \( \gamma = 2\pi |\kappa(\omega_0)|^2 D(\omega_0) \) the decay constant. Thus, a linear time-dependent term appearing beyond the leading order of the decay constant becomes important if \( |(\bar{n}_S(t) - \bar{n}_R(T_R))| >> 0. \)
If the initial average energy of the system is much more than the thermal average excitation of the bath, then the time-dependent decay rate $\gamma_1(t)$ and $\gamma_2(t)$ appreciably affect the decay dynamics in an early time.

To address the notion of thermalization in our scenario, we need to calculate the time evolution of $\bar{n}_S(t) = \langle a^\dagger a(t) \rangle_S$ from Eq.(26), which is governed by the rate equation

$$-\frac{d\bar{n}_S(t)}{dt} = \gamma(\bar{n}_S(t) - \bar{n}_R(T_R))(1 + \gamma t)$$

(28)

and its solution reads

$$\bar{n}_S(t) = \bar{n}_R(T_R) + (\bar{n}_S(0) - \bar{n}_R(T_R))e^{-\gamma t(1 + \frac{\gamma}{2})}.$$

(29)

Comparing Eq.(5) with Eq.(29), we note that in the later case the decay rate is time-dependent and thermalization becomes faster due to the incorporation of the dynamical evolution of the reservoir.

Here, we note that in the high temperature approximation, Eq.(28) leads to the modified Newton’s law of cooling as

$$-\frac{dT(t)}{dt} = \gamma(T(t) - T_R) + \gamma^2(T(t) - T_R)t,$$

(30)

where the term beyond the leading order of the decay constant becomes significant if $T_0 \gg T_R$.

The Fig. shows the comparison of the plots of Eq.(2) with Eq.(30), where we note that the thermalization occurs at a faster rate. Cooling in early time is much faster than predicted by Newton’s law. As a first order correction the theory is valid upto $t < \gamma^{-1}$; for a time longer than $t \geq \gamma^{-1}$, Newton’s exponential law should be considered for thermalization. Cooling-time for reaching from 2000°C to 800°C is almost two-third in the modified dynamics of that in the Newton’s cooling law. In comparison to Newton’s law, where the time required to bring the temperature of the system above the reservoir-temperature to its half, i.e., $\frac{T(t) - T_R}{T(0) - T_R} = \frac{1}{2}$, half-thermalization time is, $t_{1/2} = \frac{\ln 2}{\gamma}$, whereas for the modified case the half-thermalization time is given by $t_{1/2} = \sqrt{1 + 2\ln^2 \gamma}$. Therefore, in the modified case also $t_{1/2}$ is independent of $(T(0) - T_R)$.
[Fig.]: The plot of Newton’s cooling law is given by Eq.(2) (Newton, solid line) and its modified form given by Eq.(30) (Modified, dashed line) with time(in $\gamma^{-1}$) for initial and final temperatures(units arbitrary), $T_0 = 2000^0C$ and $T_R = 200^0C$.

From Eq.(26), the corresponding master equation of the diagonal elements of the density matrix can be given by the loss-gain equation of population for the step-ladder model of a harmonic oscillator as

$$
\frac{dS_{ii}(t)}{dt} = \sum_{j=i\pm 1}^{\infty} \left[ W(j|i)S_{jj}(t) - W(i|j)S_{ii}(t) \right].
$$

(31)

Here the transition rates connecting only the neighbouring levels are specifically given by

$$
W(i + 1|i) = (i + 1)\gamma[1 + \{\bar{n}_R + (\bar{n}_S(t) - \bar{n}_R)\gamma t\}]
$$

$$
W(i|i + 1) = i\gamma[\bar{n}_R + (\bar{n}_S(t) - \bar{n}_R)\gamma t],
$$

(32)

which means that the $(i + 1)$-th to $i$-th state transition rate is time dependent, and vice-versa. On the top of the usual temperature-dependent rate, it depends on $\gamma t$ and on the difference in temperature of the reservoir from that of the instantaneous temperature of the system, $T_S(t) - T_R$ (or equivalently $(\bar{n}_S(t) - \bar{n}_R)$). Usually we consider $\gamma t < 1$ for the first-order
perturbative effect. A direct consequence of the loss-gain-type master equation shows that the bath-induced forward and backward rates are modified by a factor of $\bar{n}_R + (\bar{n}_S(t) - \bar{n}_R)\gamma t$ instead of $\bar{n}_R$. As the modification arises due to the system-induced dynamics of the reservoir, which is considered as a first-order effect, we can safely assume that the rate is primarily governed by the factor $\bar{n}_R$ and therefore we can consider $(\bar{n}_S(t) - \bar{n}_R)\gamma t \leq \bar{n}_R$. This amounts to the fact that the initial system temperature should not be arbitrarily high compared to the temperature of the reservoir. Otherwise, a strong non-equilibrium evolution of the bath will produce a nonlinear coupled dynamics of system and bath variables, which is immensely difficult problem to tackle to provide any tangible physical result.

**IV. Conclusion**

In this paper we have developed the quantum theory of cooling of a system with large energy content when the reservoir has also a dynamical evolution rather than thermal equilibrium. It is explicitly demonstrated for such system that the thermal equilibrium is attained much faster than in comparison to the case of exponential decay when the reservoir is at equilibrium. Our study reveals that, the larger is the initial photon number content of the system, the faster is the rate of cooling. Possible modification of the Newton’s classical law of cooling beyond the leading order of the decay constant is pointed out and it is shown that the higher order term becomes significant if the difference between the average energy per mode of the system and the reservoir is considerable. The analysis is strictly valid for a very short time, $t < \gamma^{-1}$, and initial temperature or average energy of the system is not too much higher compared to the reservoir as the modification in the theory arises due to first order perturbation effect. We have also considered a repeated neglect of off-diagonal terms corresponding to bath degrees of freedom arising from the dynamics where only the diagonal elements of the bath density are modified in time. A faster thermalization or faster cooling is qualitatively understandable as the bath is interacting with the system more actively instead of passively waiting in its equilibrium distribution in the usual approach.

To treat a finite size [18,19] of the bath, one immediate choice is to restrict the number
of modes in the bath. This is equivalent to a pronounced recurrence of population of the vibrational states due to the back and forth exchange of energy between the modes of the system and bath. However, in our approach we have assumed the fact that the system experiences a feedback due to the dynamical evolution of the bath, but ultimately the bath is assumed to be in thermal equilibrium. We have calculated the two-point and four-point correlation functions of the bath variables by averaging over the thermal equilibrium distribution instead of a non-equilibrium distribution of the bath. The population decay is non-exponential due to this, which has simple dependence on the difference between the average energy of each mode from the time-dependent state of the system to the bath at equilibrium. A more systematic approach to treat finite size of the bath is under consideration which will be published elsewhere.

In the midst of several currently interesting coherent cooling mechanism of atoms and molecules induced by laser, this incoherent mechanism of vibrational cooling may find it worthwhile because of the huge availability of nano-materials [20] which can support a large number of degrees of freedom. It can effectively act as a bath as well as a finite quantum system to reciprocates energy with a subsystem of interest which is composed of a single or a few modes of vibration. Other associated aspects of the system-reservoir formalism require careful scrutiny in the light of the dynamical evolution of the reservoir proposed here.

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Appendix

In this appendix we shall derive the four-point reservoir correlation functions appearing in Eq. (21). The four-point reservoir correlators can be expressed in terms of two-point correlators by using the identity,

\[ \langle O_a O_b O_c O_d \rangle_R = \langle O_a O_b \rangle_R \langle O_c O_d \rangle_R + \langle O_a O_c \rangle_R \langle O_b O_d \rangle_R + \langle O_a O_d \rangle_R \langle O_b O_c \rangle_R. \]  

(A.1)

Using Eq. (A.1) let us calculate the term in the square bracket of Eq. (21) with \( i = 1, j = 2 \) and \( l, m \) runs from 1 to 2,

\[
\sum_{l,m}[\langle F_1(t)F_2(t')F_1(t_1)F_2(t_2) \rangle_R - \langle F_1(t_1)F_1(t)F_2(t')F_2(t_2) \rangle_R] \langle Q_l Q_m \rangle_S \\
+ [\langle F_2(t_2)F_1(t)F_2(t')F_1(t_1) \rangle_R - \langle F_2(t_1)F_2(t_2)F_1(t)F_1(t') \rangle_R] \langle Q_m Q_l \rangle_S = \\
[\langle F_1(t)F_2(t') \rangle_R \langle F_2(t_2)F_1(t) \rangle_R - \langle F_1(t)F_2(t_2) \rangle_R + \\
\langle F_1(t)F_2(t_2) \rangle_R \langle F_2(t')F_1(t_1) \rangle_R - \langle F_1(t_1)F_2(t') \rangle_R] \langle Q_1 Q_2 \rangle_S \\
[\langle F_2(t_1)F_1(t_1)F_2(t') \rangle_R - \langle F_2(t')F_1(t_1) \rangle_R + \\
\langle F_2(t_2)F_1(t_2) \rangle_R \langle F_1(t_2)F_2(t_1) \rangle_R - \langle F_2(t_1)F_1(t_2) \rangle_R] \langle Q_2 Q_1 \rangle_S. 
\]

(A.2)

To obtain the above equation we have neglected the off-diagonal terms, since the reservoir assumed to be a thermal one. Substituting Eqs. (13), (20a) and (20b) in Eq. (A.2), the straightforward simplification yields

\[
\sum_{l,m}[\langle F_1(t)F_2(t')F_1(t_1)F_2(t_2) \rangle_R - \langle F_1(t_1)F_1(t)F_2(t')F_2(t_2) \rangle_R] \langle Q_l Q_m \rangle_S \\
+ [\langle F_2(t_2)F_1(t)F_2(t')F_1(t_1) \rangle_R - \langle F_2(t_1)F_2(t_2)F_1(t)F_1(t') \rangle_R] \langle Q_m Q_l \rangle_S = \\
- \sum_{r, s} |\kappa_r|^2 |\kappa_s|^2 e^{i(\omega_r - \omega_s)t} e^{-i(\omega_r t_1 - \omega_s t_2)} e^{-i\omega_r \tau} \\
(2 + \bar{n}_R(\omega_r) + \bar{n}_R(\omega_s)) \langle Q_1 Q_2 \rangle_S - (\bar{n}_R(\omega_r) + \bar{n}_R(\omega_s)) \langle Q_2 Q_1 \rangle_S, 
\]

(A.3)

where \( t' \) is replaced by \( t - \tau \). Finally substituting Eq. (A.3) in Eq. (21) we obtain Eq. (22).
References

[1] C Cohen-Tannoudji and W D Phillips, Phys. Today 43, 33 (1990)

[2] C Cohen-Tannoudji, Phys. Rep. 219, 153 (1992) and references therein.

[3] C Gabbinini and A Fioretti in Trapped Particles and Fundamental Physics, Ed S N Atutov, R Calabrese and L Moi, (Kauwar Academic Press, London, 2002) pp181 and references therein.

[4] W H Louisell, Quantum Statistical Properties of Radiation (Wiley, New York, 1973) pp 336

[5] M Orszag, Quantum Optics (Springer, Heidelberg, 2000) pp 9

[6] A. A. Villaeyys, J. C. Vallet and S. H. Lin, Phys. Rev. A 43, 5030 (1991)

[7] N G van Kampen Phys. Rep. 24, 171 (1976)

[8] S Mukamel, I Oppenheim and J Ross, Phys. Rev. A17, 1988 (1978)

[9] P Ullersma, Physica 32, 27, 56, 74, 90 (1996)

[10] G Gangopadhyay and D S Ray, Phys. Rev. A44, 2206 (1991)

[11] G Gangopadhyay and D S Ray, Phys. Rev. A46, 1507 (1992)

[12] G Gangopadhyay and S Ghosal, Chem Phys Lett 289, 287 (1999)

[13] P C Brecker, H L Fragnito, J Y Bigot, C H Britocruz, C V Shank, Phys, Rev. Lett. 63, 505 (1973)

[14] W Vogel, D G Welsch, W Wilhelmi, Phys. Rev. A37, 3825 (1988)

[15] P Tchenio, A Debarre, J C Keller, J L Le Gouet, Phys Rev Lett 62, 415 (1989)
[16] M P Winters and P E Toschek, Phys Rev Lett 65, 3116 (1990)

[17] H Walther, Phys Rep 219, 263 (1990)

[18] I Andrianov and P Saalfrank, Chem Phys Lett 433, 91 (2006)

[19] M H Beck, A Jackle, G A Worth, and H D Meyer, Phys. Rep. 324, 1 (2000)

[20] See, for example, G Cao, Nanostructures and Nanomaterials: Synthesis, Properties and Application(Imperial College Press, London, 2004) and references therein.