



Reservoir effects on the temperature dependence of the relaxation to equilibrium of three simple quantum systems

A.A. Ierides*, V.M. Kenkre

Department of Physics and Astronomy, University of New Mexico, Albuquerque, NM 87131, United States

HIGHLIGHTS

- Results include nonmonotonicity of relaxing observables, e.g. energy, when T is changed.
- The effect appears only under strong interactions and is directly observable in principle.
- Useful procedures developed: a half-Markoffian approximation and a relaxation memory/rate.

ARTICLE INFO

Article history:

Received 21 November 2017

Received in revised form 22 February 2018

Available online 1 March 2018

Keywords:

Approach to thermal equilibrium

Nonmonotonic temperature dependence

Multiphonon

Single-phonon

Vibrational relaxation

Polaronic transformation

ABSTRACT

The approach to thermal equilibrium of each of three simple quantum systems in interaction with a reservoir is analyzed by calculating the time evolution of an observable appropriate for each system. Two types of interaction with the reservoir are considered: a single-phonon modulation of the interaction matrix element and a multiphonon interaction arising from a polaronic transformation for a given single-phonon, but strong, modulation of energy or frequency. The methodology employed is a recent formalism based on a coarse-grained generalized master equation. Interesting results are obtained for the multiphonon case including a nonmonotonic dependence of the time-dependent observables in the multiphonon system as the temperature is varied. Such a result does not appear in the single-phonon case, *i.e.*, for weak coupling. In addition to contributing towards the understanding of the detail in the approach to thermal equilibrium, the analysis has *practical* applications to the vibrational relaxation of molecules embedded in phonon baths and to the transport of charge in crystals subjected to electric fields strong enough to lead to the formation of Stark ladders.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction and tools of this theoretical investigation

The purpose of this paper is to analyze the process of the approach to equilibrium of three simple but typical quantum systems in interaction with a specified thermal reservoir and to describe interesting features that arise when the interaction is strong. Approach to equilibrium is one of the subjects universally considered central in statistical mechanics [1–5] and worthy of careful investigation. The three systems considered for analysis in the present paper are a nondegenerate quantum dimer [6] which can exist in one of two energetically inequivalent states, differing in energy by 2Δ ; a charged particle under the action of an applied strong electric field [7–10] E , moving across a 1-dimensional crystal of lattice constant, a ; and a harmonic oscillator of frequency Ω representing a molecule relaxing vibrationally [11,12] as a result of its interaction with the reservoir [13]. The reservoir is a set of bosons, for instance phonons, of average frequency ω_0 and dispersion σ . The

* Corresponding author.

E-mail addresses: aierides@unm.edu (A.A. Ierides), kenkre@unm.edu (V.M. Kenkre).

dimensionless coupling constant g determines the strength of the interaction between system and reservoir and is taken to lie between 0.02 and 2, depending on the coupling strength regime being studied, as described below.

The time-dependent observables calculated in order to study the approach to equilibrium are, in the first case, the occupation probability difference $p(t) = P_1(t) - P_2(t)$ of the dimer states which, from an initial value of 1 at the start, settles into the Boltzmann ratio, $-\tanh(\beta\Delta)$, where (and henceforth) $\beta = 1/k_B T$ with k_B the Boltzmann constant and T the temperature; in the second case, the velocity $v(t)$ of the electric charge q , as it speeds in the direction of the applied field; and in the third case, the average energy of the relaxing molecule $E(t) = \hbar\Omega (\langle M \rangle + 1/2)$, where $\langle M \rangle$ is the average number of excitations in the oscillator. The parameters involved in all three cases are, in addition to the temperature T and the coupling constant g , the following: the dispersion of the bath phonons, $\sigma \ll \omega_0$, and the characteristic energy of each system, 2Δ for the dimer, $\varepsilon = qEa$ for the moving charge, and $\hbar\Omega$ for the harmonic oscillator.

The tools that we use for our theoretical investigation are based on generalized master equations (GMEs) derived by extending the methodology of Zwanzig [14–16] to include coarse-graining [10,17,18]. We refer the reader to Refs. [6,10,19] for the derivation of the form of these GMEs, but display them immediately below for use in our subsequent calculations in the present paper.

As stated above, each of the three systems is characterized by a single energy. It is the difference 2Δ between the two dimer state energies in the first system, and the difference between nearest neighboring states for the other systems, ε for the second and $\hbar\Omega$ for the third. For all three systems, the reservoir contributes to the respective GME an energetically “downward” memory $\phi_-(t)$ and an “upward” memory $\phi_+(t)$, decided solely by the reservoir. The $t = 0$ to ∞ time integrals of these memories are in a detailed balance ratio to each other, $\int_0^\infty ds \phi_-(s) / \int_0^\infty ds \phi_+(s) = e^{\beta\hbar\Omega}$, the characteristic frequency of the specified system being represented by Ω .

For the dimer, the occupation probabilities $P_1(t)$ and $P_2(t)$ of the two states obey

$$\frac{dP_1(t)}{dt} = F_{21} \int_0^t ds [\phi_+(t-s)P_2(s) - \phi_-(t-s)P_1(s)], \quad (1a)$$

$$\frac{dP_2(t)}{dt} = F_{21} \int_0^t ds [\phi_-(t-s)P_1(s) - \phi_+(t-s)P_2(s)], \quad (1b)$$

where F_{21} is the relaxation rate corresponding to the energetically downward interstate transition. Here, 1 denotes the higher energetic state, and $F_{12}/F_{21} = \exp(-2\Delta/k_B T)$, satisfy the detailed balance condition. The dynamics of the charge under the influence of a strong electric field are governed by the GME

$$\begin{aligned} \frac{dP_M(t)}{dt} = & \kappa \int_0^t ds [\phi_-(t-s)P_{M+1}(s) + \phi_+(t-s)P_{M-1}(s)] \\ & - \kappa \int_0^t ds [\phi_-(t-s) + \phi_+(t-s)] P_M(s), \end{aligned} \quad (2)$$

where κ is the charged particle relaxation rate, similarly the transition rate in the direction of the external field.¹ For the relaxing molecule represented by a harmonic oscillator, the occupation probability of the oscillator state M is governed by the GME described by

$$\begin{aligned} \frac{dP_M(t)}{dt} = & \kappa \int_0^t ds \left\{ \phi_-(t-s) [(M+1)P_{M+1}(s) - MP_M(s)] \right. \\ & \left. - \phi_+(t-s) [(M+1)P_M(s) - MP_{M-1}(s)] \right\}, \end{aligned} \quad (3)$$

where κ is the downward transition rate which we will call the oscillator relaxation rate. The level spectrum is discrete in all cases, being finite (spanning only two states) in the first, infinite in the second (M 's are integers from $-\infty$ to ∞), and semi-infinite (M 's are positive integers extending from 0 to ∞) in the third system, respectively.

The GMEs in Eqs. (1)–(3), although slightly different in form as a result of the characteristics of each system, all have in them memories $\phi_\pm(t)$ which are identical because we treat identical baths influencing the systems. The difference between the GMEs arises in the terms multiplying the $\phi(t)$'s due to the respective system properties. The multiplicative terms are the corresponding relaxation rates, F_{21} for the dimer, κ for the charged particle, and κ (as well as site-index dependent terms) for the harmonic oscillator.

The present paper is organized as follows. In Section 2, brief comments are made about the form of the interaction analyzed and bath correlation functions common for all three systems are calculated along with expressions for the memories $\phi_\pm(t)$. The discussion is presented in the detailed context of the third system, the relaxing molecule, and results are used for all three cases without repeating the detail. In the next three sections, the relevant observable for each system is analyzed and the results are discussed. Concluding remarks are presented in the last section.

¹ In writing Eq. (2) we have corrected a minor sign error in Ref. [10].

Download English Version:

<https://daneshyari.com/en/article/7375189>

Download Persian Version:

<https://daneshyari.com/article/7375189>

[Daneshyari.com](https://daneshyari.com)