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Microscopic derivation of the Keilson–Storer master equation

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ABSTRACT

We consider a classical particle bilinearly coupled to a harmonic bath. Assuming that the evolution of the particle is monitored on a timescale which is longer than the characteristic bath correlation time, we derive a Markovian master equation for the probability density of the particle. The master equation is fully specified by the time correlation function of the momenta of the particle. We find the functional form of the momentum correlation function which yields the Keilson–Storer master equation (Keilson and Storer, 1952). We show that the parameters of this master equation can directly be related to the characteristic memory time of the bath.

1. Introduction

As Richard Feynman aphoristically wrote [1], the Boltzmann equilibrium distribution "is the summit of statistical mechanics, and the entire subject is either the slide-down from the summit, as the principle is applied to various cases, or the climb-up to where the fundamental law is derived and the concept of thermal equilibrium and temperature T clarified".

In the present work, we embark on this climb by deriving the master equation for the simplest case, a free classical point particle of mass m with position x and momentum p in a dissipative environment. We postulate that the time evolution of the probability density function $\rho(p,t) = \int dx \rho(x,p,t)$ is described by the master equation

$$\partial_t \rho(p,t) = -\nu\rho(p,t) + \nu \int dp' T(p|p')\rho(p',t). \tag{1}$$

Here ν is a relaxation rate and $T(p|p')$ is the relaxation kernel, which is normalized and obeys detailed balance. Different functional forms of the kernel $T(p|p')$ specify different relaxation mechanisms [2]. The two most common choices are the strong collision model corresponding to $T(p|p') = \rho_T(p)$ ($\rho_T(p)$ being the Boltzmann equilibrium distribution) and the Fokker–Planck equation, which is obtained by an expansion of $\rho(p',t)$ in the master equation (1) into a Taylor series around $p' = p$ and truncating the so-obtained Kramers–Moyal expansion at second order [3].

A widely used and versatile choice is the Keilson–Storer (KS) kernel [4]

$$T^{\mathrm{KS}}(p|p') = \frac{1}{\sqrt{2\pi m k_B T(1-\gamma^2)}} \exp\left(-\frac{(p-\gamma p')^2}{2mk_B T(1-\gamma^2)}\right). \tag{2}$$

Here k_B is the Boltzmann constant, T is the temperature of the environment, and the parameter $-1 \leqslant \gamma \leqslant 1$ determines various relaxation mechanisms. The Fokker–Planck equation is recovered in the limit $\gamma \to 1, \nu \to \infty$ and $\nu(1-\gamma) \to \xi = \text{const}$. The strong collision model is recovered if $\gamma = 0$. If $0 \leqslant \gamma \leqslant 1$, the KS kernel describes the relaxation mechanisms which are intermediate between the strong collision model and the Fokker–Planck equation. Negative γ corresponds to a preferential reversal of the momentum upon "collision", and the master equation with $\gamma = -1$ describes the so-called dichotomous or telegraph processes.

The KS model found a variety of applications. It was used, for example, to describe the effect of collisions on lineshapes [5], to elucidate non-Markovian [6] and non-Gaussian [7] effects in relaxation processes, to calculate transport coefficients [8], to study rotational relaxation [9–12], rotation-translational relaxation [13], and activated processes in condensed phases [14–16]. Multidimensional generalizations of the KS kernel have also been suggested [17,18].

According to Feynman, the "climbing up the summit" is not completed by writing down a master equation with a certain kernel. Indeed, the KS kernel (2) is merely postulated, but has not been derived. Of course, one can evaluate the rate ν and the relaxation parameter γ by considering binary collisions of rigid bodies [19–22]. For example, the KS kernel can be obtained from the venerable Rayleigh piston model [23]. Yet, this requires additional approximations. That is why the authors of Ref. [8] have remarked that the KS kernel is not a physically correct kernel since it cannot be derived from a Boltzmann-like equation. On the other

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hand, the applicability of the KS master equation is by no means restricted to dilute gases. It can be used to describe, for example, reorientation of molecules in liquid water [24], which cannot be viewed as a sequence of binary collision events. The question is whether the KS master equation has a microscopic underpinning and whether it can be derived within the general system-bath approach of statistical mechanics [25–27].

The aim of the present work is to show that the KS master equation can be derived analytically in the case of a classical particle bilinearly coupled to a harmonic bath. We speak of the point particle for the sake of definiteness only. The results remain true for the description of rotational motion, if the mass m and momentum p are replaced by the moment of inertia and the angular momentum, respectively.

2. Nakajima–Zwanzig master equation

2.1. General expressions

Let us consider a free classical particle bilinearly coupled to a classical harmonic bath. The total Hamiltonian H can be partitioned into the system (S) Hamiltonian, the bath (B) Hamiltonian, and their coupling,

$$H = H_S + H_B + H_{SB}, \tag{3}$$

where

$$H_S = \frac{p^2}{2m}. \tag{4}$$

The bath is an ensemble of classical harmonic oscillators, and the system-bath coupling is bilinear:

$$H_{SB} + H_B = \frac{1}{2}\sum_i \left(\frac{p_i^2}{m_i} + m_i\omega_i^2 \left(x_i - \frac{c_i}{m_i\omega_i^2} x \right)^2 \right). \tag{5}$$

Here x is the position of the system particle, x_i, p_i, m_i, and ω_i are the positions, momenta, masses, and frequencies of the bath oscillators, and c_i are the system-bath coupling coefficients. The influence of the bath on the system dynamics is fully determined by the bath correlation function [26,27]

$$g(t) = \frac{1}{m}\sum_i \frac{c_i^2}{m_i\omega_i^2} \cos\{\omega_i t\}. \tag{6}$$

The harmonic bath with bilinear system-bath coupling is a standard model in statistical mechanics. It is equivalent to the description in terms of the generalized Langevin equations [26,27]. The Hamiltonian (5) can be derived from the general many-body Hamiltonian by an instantaneous normal mode analysis [28,29].

The Liouville equation for the total (system-plus-bath) probability density function $\rho_{tot}(t)$ reads

$$\partial_t \rho_{tot}(t) = -i\mathcal{L}\rho_{tot}(t), \tag{7}$$

where the total Liouvillian is defined as

$$i\mathcal{L} \equiv \frac{p}{m}\partial_x + \mathcal{F}\partial_p + \sum_i \left(\frac{p_i}{m_i}\partial_{x_i} - \mathcal{F}_i\partial_{p_i} \right). \tag{8}$$

Here $\mathcal{F}$ defined as

$$\mathcal{F} = \sum_i c_i\mathcal{F}_i, \quad \mathcal{F}_i = \left(x_i - \frac{c_i}{m_i\omega_i^2} x \right) \tag{9}$$

is the total force exerted on the system by the bath oscillators.

The initial condition to Liouville equation (7) is chosen as

$$\rho_{tot}(0) = \rho_0\rho_{eq}. \tag{10}$$

Here ρ_0 is an arbitrary distribution in the system momentum space and

$$\rho_{eq} = Z_{eq}^{-1} \exp\left(-\frac{H_{SB} + H_B}{k_B T} \right) \tag{11}$$

is the equilibrium distribution of the bath in the presence of the system, Z_{eq} being its partition function.

Note that ρ_{eq} of Eq. (11) depends on x through the system-bath coupling and accounts for initial system-bath correlations. We prefer to work with this correlated initial distribution due to the following two reasons. First, it is more physical than the (commonly used) uncorrelated initial system-bath distribution $\rho_0\rho_{eq}(x=0)$. A general discussion of the importance of system-bath correlations can be found in Refs. [30–32]. Second, the correlated initial distribution (10) and (11) guarantees that the stochastic force $f(t)$ generated by the Hamiltonian (3) in the generalized Langevin equation (see Section A.3 in Appendix) possesses zero mean, $\langle f(t)\rangle = 0$. See chapter 3 of the monograph [27] and Ref. [33] for a discussion of these issues.

We introduce the projection operator [30,31]

$$\mathcal{P} \equiv \rho_{eq}\int d\mathbf{p}d\mathbf{x} \tag{12}$$

($\mathbf{p}$ and $\mathbf{x}$ denote collectively the momenta and positions of the bath oscillators) which projects the total system-plus-bath probability density function onto the correlated initial system-bath distribution (11). $\mathcal{P}$ involves the system coordinate x and differs from the "purely bath" projection operator $\mathcal{P}_B = \mathcal{P}|_{x=0}$ frequently used in the literature.

The application of the Nakajima–Zwanzig formalism [26,27,30] to Eq. (7) yields a formally exact non-Markovian master equation for the probability density function of the particle,

$$\partial_t \rho(p,t) = \int_0^t dt' \mathcal{R}_p(t-t')\rho(p,t'). \tag{13}$$

The relaxation operator in Eq. (13) can be written as a generalized Fokker–Planck operator [30],

$$\mathcal{R}_p(t) = \partial_p \mathcal{G}(t)\left(\partial_p + \frac{p}{mk_BT} \right). \tag{14}$$

Here

$$\mathcal{G}(t) = \int d\mathbf{p}d\mathbf{x}\mathcal{F}e^{-i(1-\mathcal{P})\mathcal{L}t}\mathcal{F}\rho_{eq} \tag{15}$$

is the force–force correlation operator. It follows from Eq. (14) that the relaxation operator is normalized

$$\int dp\mathcal{R}_p(t) = 0 \tag{16}$$

and obeys detailed balance

$$\mathcal{R}_p(t)\rho_T = 0, \tag{17}$$

which guarantees that $\rho(p,t)$ attains (at $t \to \infty$) the Boltzmann equilibrium distribution

$$\rho_T(p) = \frac{1}{\sqrt{2\pi mk_BT}} \exp\left(-\frac{p^2}{2mk_BT} \right). \tag{18}$$

2.2. Markovian limit

Let us assume that the characteristic relaxation time τ_B of the bath correlation function (6) is short on the timescale τ_S of the system dynamics. If we are interested in the evolution of the particle for $t \gg \tau_B$, we can extend the time integration in Eq. (13) to infinity and expand the probability density in a Taylor series,

$$\rho(p,t') = \rho(p,t) + \partial_t\rho(p,t)(t'-t) + \dots, \tag{19}$$