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Semiclassical non-Markovian Brownian motion in anharmonic potentials

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ABSTRACT

The combination of an exact stochastic decomposition of non-Markovian dissipative quantum dynamics with the semiclassical initial value formalism is applied to Brownian motion in a Morse potential. The unified sampling of the stochastic noise and the semiclassical phase space distribution introduced in Koch et al. [W. Koch, F. Grossmann, J.T. Stockburger, J. Ankerhold, Non-Markovian semiclassical dynamics, Phys. Rev. Lett. 100 (2008) 230402] is laid out here in detail. By comparing our numerical results to those obtained by using the Caldeira–Leggett master equation, we show that even in the challenging regime of moderate friction and at low temperatures, where reservoir fluctuations are clearly non-Markovian, this approach allows for the accurate description of dissipative dynamics over many oscillation periods until thermalization is reached.

1. Introduction

In the last decades the non-equilibrium dynamics of open quantum systems has been in the focus of interest in many branches of physics and chemistry [1,2]. The coupling of a (small) system of interest to a (large) environment is central to such diverse fields as quantum optics, interaction with phonons in solid state physics, chemical reactions in solution, and tunneling in biosystems, to name but a few. From a theoretical point of view, particularly cases in which perturbative approaches reach their limits have been in the focus. In addition, in recent years considerable interest has been stimulated by experimental progress which allows for the tailoring and manipulation of quantum matter on ever larger scales. In mesoscopic physics, for instance, superconducting circuits have been realized to observe coherent dynamics and entanglement [3]. Similar advance has been achieved on molecular scales with the detection of interferences in wave packet dynamics and the control of the population of specific molecular states [4]. These systems are in contact with a large number of environmental degrees of freedom, e.g., electromagnetic modes of the circuitry or vibronic modes of a rare gas cage surrounding a small molecule [5], which give rise to substantial modifications of the dynamics through relaxation and decoherence [6]. These effects are not always intuitive, as evidenced by the observation of surprisingly long sustained coherence in a Schrödinger cat type experiment [5].

The standard way to obtain the reduced dynamics of the small system of interest is tracing out "reservoir" degrees of freedom from the conservative system-plus-reservoir dynamics, using, e.g., projection operator techniques [7]. This program can also be carried out using exact path integral expressions for the reduced density matrix along the lines of Feynman and Vernon [8]. Due to its non-perturbative nature, the path integral approach became widely used in the 1980s [9–12]. The central feature of dissipative path integrals is an influence functional which describes self-interactions *non-local* in time. Hence, a simple quantum mechanical analogue to the classical Langevin equation is not known; commonly used equations, such as Master/Redfield equations [2] in the weak-coupling case and quantum Smoluchowski equations [13] for reservoir-dominated dynamics, rely on perturbation theory. Quantum Monte Carlo techniques have been put forward for tight-binding systems with strong to intermediate dissipative coupling. However, the achievable propagation times are severely limited by the dynamical sign problem [14]. Strong reservoir fluctuations alleviate this problem and make this method viable for systems in which quantum coherence decays rapidly.

In recent work, it has been shown that the dissipative dynamics described by Feynman and Vernon can be exactly reproduced through stochastic Liouville–von Neumann (SLN) equations *without* explicit memory [15,16]. This formulation turns out to be particularly efficient for weak to moderate friction and low temperatures [15,17], a regime which extends beyond the strict validity of Redfield equations and bridges the gap to the strong-coupling case amenable to path integral Monte Carlo methods.

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However, in the simplest form of the SLN approach, the number of stochastic samples needed for a meaningful numerical result scales unfavorably with the physical time simulated. Several strategies to tackle this problem are described in Ref. [17]. For the spin-boson model a hybrid method including quantum memory terms has been demonstrated by Yan et al. [18]. A reliable and efficient, widely applicable method to tackle the dissipative dynamics for continuous systems in non-perturbative parameter regimes was first presented in Ref. [19] and termed semiclassical Brownian motion (SCBM) in Ref. [20].

In the present paper, we give a detailed account of the methodology introduced in [19] and apply it to a nonlinear test system. We show explicitly how we combine the exact stochastic Schrödinger formulation with the semiclassical initial value representation (IVR) of the quantum mechanical propagator of Herman and Kluk (HK) [21,22], which has seen an impressive number of applications ranging from atomic [23] to chemical physics [24–26] after the work of Kay [27] stimulated renewed interest in the approach. We note that a direct stationary-phase evaluation of the double path integral for the reduced density is not a consistent semiclassical approximation [1] or may involve additional approximations [28]. An average over *thermal* fluctuations, which generally do not admit a Gaussian approximation, is implicit in the reduced density matrix. The proper classical limit is given by a generalized Langevin equation, which treats thermal fluctuations explicitly. Instead of a single pair of stationary-phase trajectories, a statistical ensemble of such pairs is needed. We note that efforts are currently under way to extend the semiclassical initial value approach to dynamics with quantum memory effects [29,30].

Here, however, we will use a memory-free representation, which accounts for non-Markovian reservoir fluctuations[1] entirely through correlations of complex-valued noise forces. Our central finding is that this combination of stochastic and semiclassical methods provides a consistent semiclassical formulation of quantum dissipation. We will show that a combined sampling strategy provides a numerical method which significantly outperforms fully quantum mechanical stochastic methods, allowing computations up to times at which equilibrium is reached.

The paper is organized as follows: In Section 2, we review the stochastic approach used in the remainder of the presentation. In Section 3 the semiclassical HK propagator is discussed together with its underlying stochastic classical dynamics. After a brief review of the Caldeira–Leggett master equation in Section 4 and of the Morse oscillator model in Section 5, our combined sampling strategy is laid out in detail in Section 6. The results gained with that numerical strategy for the damped Morse oscillator are presented and discussed in Section 7. We also compare some of our results to those obtained from the Caldeira–Leggett master equation to point out the non-Markovian character of our approach. Finally, a summary and an outlook are given in Section 8.

2. Stochastic unraveling of influence functionals

We start our description of an open quantum system in the standard way [1] by formally including a heat bath in a Hamiltonian

$$\widehat{H} = \widehat{H}_S + \widehat{H}_B + \widehat{H}_I, \tag{1}$$

which is a sum of three terms representing a distinguished system, a heat bath, and the interaction of the system with the thermal reservoir. For simplicity we treat the case of a single degree of freedom x here, and the case of a separable coupling proportional to x. The corresponding fluctuating force from the reservoir is assumed to have Gaussian statistics. (This property may result either from the central limit theorem or from intrinsically linear dynamics of the heat bath.)

If the heat bath and the system are initially uncorrelated, one derives a path integral expression for the time-evolved reduced density matrix of the form [8,31,1]

$$\rho(x_f, x_f', t) = \int dx_i\, dx_i' \rho(x_i, x_i', 0) \times \int \mathscr{D}[x_1]\mathscr{D}[x_2] \times \exp\left\{\frac{i}{\hbar}(S_S[x_1] - S_S[x_2])\right\} \times F[x_1, x_2], \tag{2}$$

where the two real-time paths x_1 and x_2 run in time t from x_i and x_i' to x_f and x_f', respectively. In addition to the usual exponentiated action, a non-separable *influence functional* F appears, in which all modifications of the dynamics due to the fluctuations and the time-dependent response of the heat bath are summed up. Switching from x_1 and x_2 to center-of-mass and difference coordinates $r = (x_1 + x_2)/2$ and $y = x_1 - x_2$, the influence functional can be given the compact form $F[y, r] = \exp(-\Phi[y, r]/\hbar)$ with

$$\Phi[y, r] = \frac{1}{\hbar}\int_0^t du \int_0^u dv\, y(u)\left[L'(u - v)y(v) + 2iL''(u - v)r(v)\right] + i\mu\int_0^t du\, y(u)r(u). \tag{3}$$

The complex-valued friction kernel $L(t) = L'(t) + iL''(t)$ is related to the force–force auto-correlation function of the bath and is completely determined by its spectral density $J(\omega)$ and inverse temperature β according to

$$L(t) = \frac{\hbar}{\pi}\int_0^\infty d\omega J(\omega)\left[\coth\frac{\hbar\beta\omega}{2}\cos\omega t - i\sin\omega t\right]. \tag{4}$$

For a Markovian environment, the real and imaginary parts of $L(t)$ may be approximated by multiples of the Dirac delta function and its derivative, respectively. The static susceptibility denoted by $\mu = -\int_0^\infty du L''(u)/(2\hbar)$ is a property of the reservoir.[2]

In Ref. [16] it was shown that a stochastic unraveling of the forward and the backward paths can be given in the form

$$\rho(x_f, x_f', t) = \int dx_i \int dx_i' \rho(x_i, x_i', 0) \times M[K_{z_1}(x_f, t; x_i, 0) \times (K_{z_2}(x_f', t; x_i', 0))^*], \tag{5}$$

where M denotes the average over stochastic forces z_j $(j = 1, 2)$ with suitably chosen correlation functions (see below). This random noise modifies the system action terms; the action to be used in the path integral expressions of the respective propagators K_{z_j} is

$$S_{z_j}[x_j] = S_S[x_j] - \frac{\mu}{2}\int_0^t du x_j(u)^2 + \int_0^t du z_j(u)x_j(u). \tag{6}$$

The present stochastic approach differs from a similar one by Strunz et al. [32] through the appearance of *two* noise variables, allowing for the elimination of quantum memory effects in addition to the stochastic unraveling.

The relative simplicity of Eq. (6) allows the dynamics of the reduced density matrix to be described in terms of a simple SLN equation [16],

$$i\hbar\frac{d}{dt}\hat{\rho} = [H_S, \hat{\rho}] - \xi[x, \hat{\rho}] - \frac{\hbar v}{2}[x, \hat{\rho}]_+ + \frac{\mu}{2}[x^2, \hat{\rho}], \tag{7}$$

where $\xi(t) = \frac{1}{2}[z_1(t) + z_2^*(t)]$ and $v(t) = \frac{1}{\hbar}[z_1(t) - z_2^*(t)]$.

[1] In the context of Brownian motion problems, a reservoir is usually considered Markovian only if its correlation time is the shortest timescale of the problem. This convention differs from the common usage of 'Markovian dynamics' in the context of quantum optics, where the weaker assumption is made that the reservoir is considered 'fast' in the interaction picture.

[2] The potential term $\mu y r$ in Eq. (3) is conventionally used in cases where the heat bath is a model for velocity-dependent friction without any static response.