Quantum Smoluchowski equation for a spin bath

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We derive the quantum mechanical description of overdamped Brownian motion of a particle in a spin bath of two-level atoms. The resulting Smoluchowski equation is used to calculate the rate of escape of the particle from a metastable state. At 0 K the decay rate is finite. We show that while quantization enhances the decay rate, higher temperatures induce thermal saturation, resulting in effective a reduction of the system-bath coupling. The role of coherence is examined.

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I. INTRODUCTION

The system-reservoir model [1–8] forms the standard microscopic basis for quantum theory of Brownian motion. The reservoir consists of a large number of degrees of freedom coupled to the system. In the overwhelming majority of the situations dealing with problems of laser and optical physics [3,4], condensed-matter physics [5–7], and chemical physics [7,8], these degrees of freedom correspond to those of harmonic oscillators, and the reservoir is bosonic in nature. If, on the other hand, the bosonic heat bath is replaced by a spin bath of, say, two-level atoms, the stochastic dynamics [9–18] of the system is governed by quantum noise and dissipation due to spin degrees of freedom. Two pertinent points are to be noted here. First, a spin-$1/2$ particle or a two-level atom amenable to theoretical description in terms of Pauli operators has no classical analog, and the spin bath is characterized by an average excitation number in the form of Fermi-Dirac statistics. Second, the governing fluctuation-dissipation relation for the spin bath does not reduce to its classical limit as a harmonic bath at high temperatures. However, for weak coupling a harmonic bath with infinite degrees of freedom constitutes almost a universal description of a real physical environment [5], and in fact its behavior merges to that of a spin bath at 0 K. Thermal properties of the two baths begin to differ at finite temperatures. One of the earliest examples of a spin bath was considered by Sargent, Scully, and Lamb [3] for describing the dynamics of a cavity mode damped by an atomic beam reservoir consisting of two-level atoms. A two-level reservoir was investigated by Shao and Hänggi [11] in a spin-spin bath model analogous to a spin-boson model. It was shown that although the two models at zero temperature do not differ significantly, an increase of temperature favors coherence in a spin bath. The differential behavior between a two-level reservoir and a harmonic bath has also been analyzed by Caldeira *et al.* [12] within the framework of Feynman-Vernon theory. They showed that the effective spectral density contains a temperature-dependent hyperbolic tangent factor which decreases with temperature, implying that at higher temperatures the effective system-bath coupling is reduced assisting emergence of coherent behavior in the dynamics. The path integral approaches to quantum stochastic processes based on system-spin reservoir models have also received attention in the context of dynamical localization [13] of a particle at low temperature, optical conductivity, and direct current resistivity for charge carriers [14] in an external force field. A spin bath has also been useful for the description [15–17] of interacting nanomagnets, a spin interacting with independent spin modes or nuclear spins through hyperfine interaction [15], and ions in liquid ^{3}He [17]. Very recently we proposed [19] a scheme for quantum Brownian motion of a particle in the presence of a spin bath of two-level atoms. This is based on the spin coherent state representation of the noise operators [20] and a canonical thermal distribution of the associated c numbers, which lead to a generalized quantum Langevin equation. The focus of the present analysis is the extension of the theory under overdamped conditions in configuration space of the quantum mechanical mean position of the particle. Our aim is to develop a quantum Smoluchowski equation for quantum noise due to spin degrees of freedom and to calculate the escape rate of the particle from a metastable state as an application. We show that the dynamics, characterized by a particle-spin bath interaction, gives rise to a temperature-dependent hyperbolic tangent factor in the effective spectral density. This factor is substantially reduced at higher temperatures due to thermal saturation. The escape rate is finite at 0 K.

The outline of the paper is as follows: In Sec. II we give an outline of the approach to quantum stochastic dynamics of a particle in a spin bath developed recently by us [19]. The main result of this treatment is a c-number description of the spin bath degrees of freedom responsible for noise and dissipative terms of the Langevin equation for the particle. In Sec. III, we derive the quantum Smoluchowski equation for the overdamped dynamics in a spin bath. A systematic scheme for quantum corrections due to nonlinearity of the system potential is given in Sec. IV, where the parameters $a = 1.0$ and $b = 0.15$ are taken for calculation. The theory is applied to derive the rate of decay out of a metastable well. The paper is concluded in Sec. V.

II. QUANTUM STOCHASTIC DYNAMICS IN A SPIN BATH

We begin with a system-reservoir model described by the following Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2} + V(\hat{q}) + \hbar \sum_k \omega_k \hat{\sigma}_k^\dagger \hat{\sigma}_k + \hbar \sum_k g_k \hat{q} \left(\hat{\sigma}_k^\dagger + \hat{\sigma}_k + \frac{g_k}{\omega_k} \hat{q} \right). \tag{2.1}$$

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Here a particle of unit mass is coupled to a set of spin-1/2 particles (two-level atoms) with characteristic frequencies ω_k. $\hat{q}$ and $\hat{p}$ are coordinate and momentum operators of the particle. The two-level bath atoms are described by a set of Pauli operators $\{\hat{\sigma}_k,\hat{\sigma}_k^\dagger$ and $\hat{\sigma}_{zk}\}$. $\hat{\sigma}_k^\dagger(\hat{\sigma}_k)$ is the creation (annihilation) operator for the kth two-level atom coupled linearly to the particle through the coupling constant g_k. The potential $V(\hat{q})$ is due to the external force field acting on the particle. $\hat{q}$ and $\hat{p}$ follow the usual commutation relation $[\hat{q},\hat{p}] = i\hbar$. The kth spin-$\frac{1}{2}$ particle or two-level atom obeys the anticommutation rule $\{\hat{\sigma}_k,\hat{\sigma}_k^\dagger\} = 1$, the associated algebra $\hat{\sigma}_k^2 = \hat{\sigma}_k^{\dagger 2} = 0$, and the commutation relations are $[\hat{\sigma}_k^\dagger,\hat{n}_k] = -\hat{\sigma}_k^\dagger$, $[\hat{\sigma}_k,\hat{n}_k] = \hat{\sigma}_k$, and $[\hat{\sigma}_k^\dagger,\hat{\sigma}_k] = \hat{\sigma}_{zk}$, where $\hat{n}_k = \hat{\sigma}_k^\dagger\hat{\sigma}_k$ is the number operator for the kth spin bath. These relations also imply $\hat{\sigma}_{zk} = 2\hat{n}_k - 1$. The presence of the counterterm $\hbar\sum_k \frac{g_k^2}{\omega_k}\hat{q}^2$ in the Hamiltonian ensures that the particle feels the potential $V(\hat{q})$ which remains unaffected by the interaction during its dynamical evolution. Thus the model is basically a spin bath analog of the Zwanzig version of a system-harmonic bath model. Eliminating the bath degrees of freedom as carried out in Ref. [19], we obtain the operator Langevin equation for the particle

$$\ddot{\hat{q}} + \int_0^t dt'\dot{\hat{q}}(t')\kappa(t-t') + V'(\hat{q}) = \hat{f}(t), \tag{2.2}$$

where the memory kernel and the noise operator are given by

$$\kappa(t-t') = 2\hbar\sum_k \frac{g_k^2}{\omega_k}\cos\omega_k(t-t') \tag{2.3}$$

and

$$\hat{f}(t) = -\hbar\sum_k g_k[\hat{S}_k(0)e^{-i\omega_k t} + \hat{S}_k^\dagger(0)e^{i\omega_k t}], \tag{2.4}$$

respectively. $\hat{S}_k^\dagger(0)$ and $\hat{S}_k(0)$ are shifted bath operators and are defined by

$$\hat{S}_k^\dagger(0) = \hat{\sigma}_k^\dagger(0) + \frac{g_k}{\omega_k}\hat{q}(0)$$

and

$$\hat{S}_k(0) = \hat{\sigma}_k(0) + \frac{g_k}{\omega_k}\hat{q}(0). \tag{2.5}$$

On the basis of the quantum mechanical average $\langle\cdots\rangle$ taken with the initial product separable quantum states of the particle and the spins at $t=0$, $|\phi\rangle|\xi_1\rangle|\xi_2\rangle\cdots|\xi_N\rangle$, where $|\phi\rangle$ denotes an arbitrary initial state of the particle and $|\xi_k\rangle$ corresponds to the initial coherent state [21] of the kth spin-1/2 particle, Eq. (2.2) can be cast into the form of a generalized quantum Langevin equation as follows:

$$\ddot{q} + \int_0^t \dot{q}(t')\kappa(t-t')dt' + V'(q) = \eta(t) + Q(q,\langle\delta\hat{q}^n\rangle). \tag{2.6}$$

Here the quantum mechanical mean value of the position operator is $\langle\hat{q}(t)\rangle = q(t)$. We further assume $q(0) = 0$, without any loss of generality. Q represents the quantum correction due to the system potential as given by

$$Q(q,\langle\delta\hat{q}^n\rangle) = V'(q) - \langle V'(\hat{q})\rangle, \tag{2.7}$$

which, by expressing $\hat{q}(t) = q(t) + \delta\hat{q}(t)$ in $V(\hat{q})$ and using a Taylor expansion around q for sufficiently smooth potential, may be rewritten as

$$Q(q,\langle\delta\hat{q}^n\rangle) = -\sum_{n\geqslant 2}\frac{1}{n!}V^{(n+1)}(q)\langle\delta\hat{q}^n\rangle. \tag{2.8}$$

V^m is the mth derivative of the potential $V(q)$ with respect to q. We will return to its calculation in the latter part of this section.

The quantum mechanical mean value of the Langevin force operator $\hat{f}(t)$ is now given by

$$\langle\hat{f}(t)\rangle = \eta(t), \tag{2.9}$$

where $\eta(t)$ is a c-number noise defined as [since $\langle\hat{q}(0)\rangle = q(0) = 0$]

$$\begin{aligned}\eta(t) &= -\hbar\sum_k g_k\{\langle\hat{\sigma}_k(0)\rangle e^{-i\omega_k t} + \langle\hat{\sigma}_k^\dagger(0)\rangle e^{i\omega_k t}\}\\ &= -\hbar\sum_k g_k\{\xi_k(0)e^{-i\omega_k t} + \xi_k^*(0)e^{i\omega_k t}\},\end{aligned} \tag{2.10}$$

where $\xi_k(0)$ and $\xi_k^*(0)$ are the associated complex c numbers. $\eta(t)$ must satisfy the noise characteristics of the spin bath at equilibrium:

$$\langle\eta(t)\rangle_s = 0, \tag{2.11}$$

$$\langle\eta(t)\eta(t')\rangle_s = \hbar^2\sum_k g_k^2\cos\omega_k(t-t')\tanh\left(\frac{\hbar\omega_k}{2KT}\right). \tag{2.12}$$

To ensure that the c-number noise $\eta(t)$ is zero centered [Eq. (2.11)] and satisfies the fluctuation-dissipation relation [Eq. (2.12)] it is necessary that $\xi_k(0)$ and $\xi_k^*(0)$ are distributed according to a thermal canonical distribution of Gaussian form as follows:

$$P[\xi_k(0),\xi_k^*(0)] = N\exp\left\{-\frac{|\xi_k(0)|^2}{2\tanh\left(\frac{\hbar\omega_k}{2KT}\right)}\right\}, \tag{2.13}$$

where N is the normalization constant. This is essentially the spin bath counterpart of the Wigner thermal canonical distribution [22] for a harmonic bath proposed recently by us [19]. The width of the distribution is given by $\tanh\frac{\hbar\omega_k}{2KT}$, which is related to the average thermal excitation number $\bar{n}_F(\omega_k)$ of the bath as $\tanh\frac{\hbar\omega_k}{2KT} = 1 - 2\bar{n}_F(\omega_k)$, with $\bar{n}_F(\omega_k)$ being the Fermi-Dirac distribution function. The statistical average $\langle\cdots\rangle_s$ over the quantum mechanical mean value of a bath operator $\langle\hat{A}_k\rangle$ which is a function of $\xi_k(0)$ and $\xi_k^*(0)$ can be defined as

$$\langle\langle\hat{A}_k\rangle\rangle_s = \int\langle\hat{A}_k\rangle P[\xi_k(0),\xi_k^*(0)]d\xi_k(0)d\xi_k^*(0). \tag{2.14}$$

We now return to the quantum operator equation (2.2) and put $\hat{q}(t) = q(t) + \delta\hat{q}(t)$ and $\dot{\hat{q}}(t) = \dot{q}(t) + \delta\dot{\hat{q}}(t)$, where $q(t) = \langle\hat{q}(t)\rangle$ and $\dot{q}(t) = \langle\dot{\hat{q}}(t)\rangle$ and by construction $[\delta\hat{q},\delta\hat{p}] = i\hbar$ and $\langle\delta\hat{q}\rangle = \langle\delta\dot{\hat{q}}\rangle = 0$. Making use of Eq. (2.6) in the resulting equation we obtain

$$\begin{aligned}\delta\ddot{\hat{q}} &+ \int_0^\infty dt'\kappa(t-t')\delta\dot{\hat{q}}(t') + V''(q)\delta\hat{q}\\ &+ \sum_{n\geqslant 2}\frac{1}{n!}V^{(n+1)}(q)[\delta\hat{q}^n(t) - \langle\delta\hat{q}^n(t)\rangle] = \delta\hat{\eta}(t),\end{aligned} \tag{2.15}$$

where $\delta\hat{\eta}(t) = \hat{f}(t) - \eta(t)$. Equation (2.15) forms the basis of the calculation of quantum mechanical correction due to nonlinearity of the system potential. It is apparent that this equation precludes the possibility of an exact solution. However, depending on the nonlinearity of the potential, the memory kernel, systematic approximations may be made. The following section is devoted to overdamped dynamics in the Markovian limit.

Summarizing the discussion, we note that the particle moving under an external potential field $V(q)$ is driven by a noise $\eta(t)$ due to the spin bath and a force due to quantum dispersion $Q(q,\langle\delta\hat{q}^n\rangle)$. The quantum nature of the dynamics is manifested through the fluctuation dissipation relation for the spin bath and the quantum dissipation term. Equations (2.6) and (2.15) are key equations that govern the stochastic dynamics of the particle.

III. OVERDAMPED DYNAMICS IN THE MARKOVIAN LIMIT: THE SMOLUCHOWSKI EQUATION

To proceed further we begin by considering the Markovian limit of the memory kernel [Eq. (2.3)] and the correlation function of the c-number noise $\eta(t)$ described by Eq. (2.12). To this end we assume [2,3] the continuum limit of the sum $\sum_k \frac{2\hbar g_k^2}{\omega_k}$ by introducing a density of modes $\rho(\omega)$ so that we may write $\frac{2\hbar g^2(\omega)\rho(\omega)}{\omega}$ as a Lorentzian function centered around a linearized static frequency ω_0 of the system, in the form $\frac{1}{2\pi}\frac{\gamma_0}{1+(\omega-\omega_0)^2\tau_c^2}$ (see Ref. [23]). γ_0 is the dissipation constant and τ_c is the correlation time of the noise. In the limit $\tau_c \to 0$, $\kappa(t-t')$ reduces to the form

$$\kappa(t-t') = \frac{\gamma_0}{2\pi}\int_{-\infty}^{+\infty} d\omega \cos\omega(t-t') = \gamma_0\delta(t-t'). \tag{3.1}$$

Proceeding in the same way we derive the Markovian limit of the correlation function $\langle\eta(t)\eta(t')\rangle_s$ as follows: We first rewrite Eq. (2.12) in the form

$$\langle\eta(t)\eta(t')\rangle_s = \sum_k \frac{2\hbar g_k^2}{\omega_k}\left(\frac{\hbar\omega_k}{2}\tanh\frac{\hbar\omega_k}{2KT}\right)\cos\omega_k(t-t'). \tag{3.2}$$

Again replacing $\frac{2\hbar g_k^2}{\omega_k}$ in the continuum limit in Eq. (3.2) as before we have

$$\langle\eta(t)\eta(t')\rangle_s = \int_{-\infty}^{+\infty} d\omega \frac{1}{2\pi}\left(\frac{\gamma_0}{1+(\omega-\omega_0)^2\tau_c^2}\right) \times \left(\frac{\hbar\omega}{2}\tanh\frac{\hbar\omega}{2KT}\right)\cos\omega(t-t'). \tag{3.3}$$

For vanishing τ_c, the distribution function around ω_0 becomes broad so that one may take the slowly varying quantity $\frac{\hbar\omega}{2}\tanh\frac{\hbar\omega}{2KT}$ out of the integration over the frequency centered at ω_0 with a value $\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}$, and we are led to the following expression for the correlation function:

$$\langle\eta(t)\eta(t')\rangle_s = \gamma_0\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\delta(t-t'). \tag{3.4}$$

Based on these considerations we are in a position to provide a probabilistic description of the stochastic dynamics in the over-damped limit. In this limit we neglect the inertial term in Eq. (2.6) and make use of expression (3.1) to obtain (see the Appendix):

$$\gamma_0\dot{q} + V'_{\text{quan}}(q,\langle\delta\hat{q}^n\rangle) = \eta(t), \tag{3.5}$$

where

$$V'_{\text{quan}}(q,\langle\delta\hat{q}^n\rangle) = V'(q) - Q(q,\langle\delta\hat{q}^n\rangle). \tag{3.6}$$

Since the system is thermodynamically closed the density is conserved, i.e., $\int\rho(q,t)dq = 1$, which ensures that any change in density with time is balanced by the divergence of a current:

$$\frac{\partial\rho}{\partial t} + \frac{\partial(\dot{q}\rho)}{\partial q} = 0. \tag{3.7}$$

Following Zwanzig [21] and using van Kampen's lemma [1] $\langle\rho(q,t)\rangle_s = P(q,t)$, where $P(q,t)$ is the probability density function, one arrives at the following equation:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q}\left(\frac{V'_{\text{quan}}}{\gamma_0}\right)P + \frac{1}{\gamma_0^2}\int_0^t dt'\langle\eta(t)\eta(t')\rangle_s e^{-[\phi(t)-\phi(t')]} \times \frac{\partial^2 P(q,t')}{\partial q^2}, \tag{3.8}$$

where $\phi(t) = -\int_0^t \frac{\partial V'}{\partial q}\frac{1}{\gamma_0}dt'$.

The use of correlation function (3.3) in Eq. (3.8) yields the Smoluchowski equation

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial q}\left(\frac{V'_{\text{quan}}}{\gamma_0}\right)P + D_f\frac{\partial^2 P}{\partial q^2}. \tag{3.9}$$

Here the diffusion coefficient of the particle in a spin bath (in the Markovian limit) is given by

$$D_f = \frac{\hbar\omega_0}{2\gamma_0}\tanh\left(\frac{\hbar\omega_0}{2KT}\right). \tag{3.10}$$

Equation (3.9) is the classical-looking Smoluchowski equation which describes the overdamped quantum dynamics of the particle in terms of a probability density function $P(q,t)$, with q being the quantum mechanical mean value of the position of the particle. Two important changes are apparent. First, the potential $V_{\text{quan}}(q,\langle\delta\hat{q}^n\rangle)$ includes the quantum corrections, in principle, to all orders. Second, $\tanh(\frac{\hbar\omega_0}{2KT})$ makes an imprint of the Fermi-Dirac character of the spin bath through the expression for the diffusion coefficient [Eq. (3.10)]. We close this section with a note that Smoluchowski equation (3.9) allows an equilibrium solution under a zero current condition as $\sim\exp(-\frac{V_{\text{quan}}(q,\langle\delta\hat{q}^n\rangle)}{D})$, where $D = \frac{\hbar\omega_0}{2}\tanh(\frac{\hbar\omega_0}{2KT})$. This is independent of the dissipation constant γ_0 and ensures thermodynamic consistency of the present scheme.

IV. DECAY OF A METASTABLE STATE IN A SPIN BATH

Although $Q(q,\langle\delta\hat{q}^n\rangle)$, in principle, includes quantum corrections to all orders, the explicit calculation of this quantity requires a suitable approximate scheme for an arbitrary potential. To this end we return to quantum correction equation (2.15) which in the overdamped limit reduces to the following form:

$$\gamma_0 \delta\dot{\hat{q}} + V''(q)\delta\hat{q} + \sum_{n\geqslant 2} \frac{1}{n!} V^{(n+1)}(q)(\delta\hat{q}^n - \langle\delta\hat{q}^n\rangle) = \delta\hat{\eta}. \tag{4.1}$$

With the help of operator equation (4.1) we obtain the equations for the quantum mechanical mean value of the corrections $\langle\delta\hat{q}^n\rangle$ in successive orders (after multiplying the operator equation with $\delta\hat{q}, \delta\hat{q}^2, \ldots$, and carrying out quantum mechanical averages with the initial product separable quantum state of the system and the coherent states of the noise operators as $|\phi\rangle\,\{|\xi_i\rangle\}$ as before):

$$\frac{d}{dt}\langle\delta\hat{q}^2\rangle = -\frac{1}{\gamma_0}[2V''(q)\langle\delta\hat{q}^2\rangle + V'''(q)\langle\delta\hat{q}^3\rangle], \tag{4.2}$$

$$\frac{d}{dt}\langle\delta\hat{q}^3\rangle = -\frac{1}{\gamma_0}\left[3V''(q)\langle\delta\hat{q}^3\rangle + \frac{3}{2}V'''(q)\langle\delta\hat{q}^4\rangle - \frac{3}{2}V'''(q)\langle\delta\hat{q}^2\rangle^2\right], \tag{4.3}$$

and so on. For a minimum uncertainty state $\langle\delta\hat{q}^2\rangle \sim O(\hbar)$, and therefore the higher-order terms of $\langle\delta\hat{q}^n\rangle$ for $n \geqslant 3$ can be neglected to calculate the leading-order correction. Second, a closer look into the correction equations (4.2) and (4.3) suggest that the quantum corrections are suppressed in successive orders by $\sim O(1/\gamma_0)$ by friction. Thus under overdamped conditions the quantum correction diminishes by $\sim O(\hbar/\gamma_0)$ at each order. This is a corroboration of the traditional wisdom that with enhancement of dissipation the system tends to lose its quantum character.

To take into account the leading-order contribution $\langle\delta\hat{q}^2\rangle$ explicitly we may thus write

$$d\langle\delta\hat{q}^2\rangle = -\frac{2}{\gamma_0}V''(q)\langle\delta\hat{q}^2\rangle dt. \tag{4.4}$$

The overdamped deterministic motion, on the other hand, gives

$$\gamma_0 dq = -V'(q)dt, \tag{4.5}$$

which when used in Eq. (4.4) yields after integration

$$\langle\delta\hat{q}^2\rangle = \Delta[V'(q)]^2, \tag{4.6}$$

where Δ is the quantum correction factor, given by $\Delta = \frac{\langle\delta\hat{q}^2\rangle_m}{[V'(q_m)]^2}$. q_m is the quantum mechanical mean position at which $\langle\delta\hat{q}^2\rangle$ is a minimum (for example, $\langle\delta\hat{q}^2\rangle_m \sim \frac{\hbar}{2\omega_0}$). With this the quantum correction up to a leading order is

$$Q = -\frac{\Delta}{2}V'''(q)[V'(q)]^2, \tag{4.7}$$

and the modified potential is given by

$$V'_{\rm quan}(q) = V'(q) + \frac{\Delta}{2}V'''(q)[V'(q)]^2. \tag{4.8}$$

It is pertinent to note that the lowest-order quantum correction does not involve any friction coefficient or temperature. Second, the inversion symmetry of the classical potential, if any, is retained.

Therefore the dynamical or equilibrium properties can be correctly calculated without any nonphysical bias or contribution using this potential. A quantity of special interest here is the escape rate of the overdamped particle from a metastable well when the particle is subjected to quantum fluctuation due to the spin bath. The time evolution of the particle is governed by the Smoluchowski equation (3.9) when the potential is given by (4.8). Under the condition that the mean escape time from the metastable well is much larger compared to the time scale of the overdamped quantum dynamics of the mean position of the particle and that the strength of the c-number noise is smaller than the barrier height, one may derive the rate of escape k using the flux-overpopulation method [7] by solving Smoluchowski equation (3.9) in the usual way to obtain

$$k = \frac{\hbar\omega_0 \tanh\frac{\hbar\omega_0}{2KT}}{2\gamma_0}\frac{1}{\int_{q_0}^{A} e^{V_{\rm quan}(q)/D}dq \int_{q_1}^{q_2} e^{-V_{\rm quan}(q)/D}dq}, \tag{4.9}$$

where $\gamma_0 D = D_f$, and the limits of integration correspond to the points referred to by the typical Kramers potential $V(q) = \frac{1}{2}aq^2 - \frac{1}{3}bq^3$ as shown in Fig. 1. The integrals in the denominator signify the contribution from the flux around the barrier top at $q_b(\int_{q_0}^{A} e^{V_{\rm quan}(q)/D}dq)$ and another from the population at the left well located at $q_0(\int_{q_1}^{q_2} e^{-V_{\rm quan}(q)/D}dq)$, with linearization of the potential $V_{\rm quan}(q)$ around q_b and q_0. Upon integration the expression for the escape rate reduces to the following form:

$$k = \frac{\omega_b\omega_0}{2\pi\gamma_0}\exp(-E_0/D)\exp\left[-\frac{\Delta}{2D}(\phi_b - \phi_0)\right], \tag{4.10}$$

where ω_0 and ω_b are the harmonic frequencies associated with the left well and the inverted well, respectively, and E_0 is the usual barrier height for the classical potential. The quantum contribution is manifested in the second exponential term where ϕ_b and ϕ_0 are given by

$$\phi_b = \int_0^{q_b} V'''(q)[V'(q)]^2 dq \tag{4.11}$$

and

$$\phi_0 = \int_0^{q_0} V'''(q)[V'(q)]^2 dq. \tag{4.12}$$

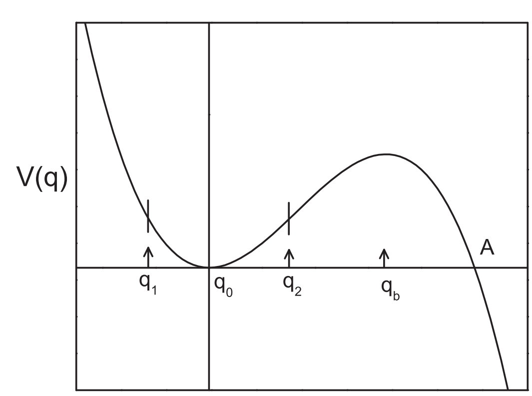

FIG. 1. A schematic plot of the cubic potential $V(q) = \frac{1}{2}aq^2 - \frac{1}{3}bq^3$, used for calculation of the decay of the metastable state.

For the given prototypical potential depicted in Fig. 1, ϕ_b and ϕ_0 reduce to $-2b\int_0^{a/b}[V'(q)]^2 dq$ and 0, respectively. The expression for the rate constant therefore assumes the following form:

$$k = \frac{\omega_b \omega_0}{2\pi\gamma_0}\exp(-E_0/D)\exp\left\{\frac{\Delta b}{D}\int_0^{a/b} dq[V'(q)]^2\right\}. \tag{4.13}$$

At zero temperature (0 K) $\tanh\frac{\hbar\omega_0}{2KT} \to 1$ and therefore we have $D(=\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}) \to \frac{\hbar\omega_0}{2}$. The dissipative spin dynamics of two-level atoms agrees well with the results obtained from the spin-boson model. This has been stressed earlier by Shao and Hänggi [11] in the context of the decoherent dynamics of a two-level system coupled to a spin bath, and by others [12]. Thus the rate constant assumes a finite form at 0 K. At low but finite temperatures, i.e., when $\frac{\hbar\omega_0}{KT} \sim 1$, the temperature-dependent factor begins to differ from unity. To gain further insight into this regime, the correlation function of c-number noise [Eq. (2.12)] may be rewritten as

$$\begin{aligned}\langle\eta(t)\eta(t')\rangle_s &= C_T(t-t')\\ &= \sum_k \frac{\hbar g_k^2}{\omega_k}\left(\hbar\omega_k \tanh\frac{\hbar\omega_k}{2KT}\right)\cos\omega_k(t-t').\end{aligned} \tag{4.14}$$

One may express the spectral density as

$$J_T(\omega) = \int_0^\infty C_T(t)\cos\omega t dt. \tag{4.15}$$

Making use of the correlation function Eq. (4.14) in Eq. (4.15) we obtain

$$J_T(\omega) = \pi\sum_k \frac{\hbar g_k^2}{\omega_k}\left\{\frac{\hbar\omega_k}{2}\tanh\frac{\hbar\omega_k}{2KT}\right\}\delta(\omega-\omega_k). \tag{4.16}$$

The expression for spectral density of similar form was derived earlier for the influence functional for a two-level bath via the second-order perturbation theory by Caldeira *et al.* [12]. The key point is the appearance of the quantity inside the braces in Eq. (4.16). We first express this quantity (say, for the kth mode) as

$$\frac{\hbar\omega}{2}\tanh\frac{\hbar\omega}{2KT} = \frac{\hbar\omega}{2} - \frac{\hbar\omega}{e^{\frac{\hbar\omega}{KT}}+1} \tag{4.17}$$

$$= -\frac{\hbar\omega}{2}\langle\hat{\sigma}_z\rangle_{\rm qs}, \tag{4.18}$$

where $\langle\hat{\sigma}_z\rangle_{\rm qs}$ is a quantum statistical average $\langle\cdots\rangle_{\rm qs}$ of Pauli operator $\hat{\sigma}_z$ and measures the population difference between the two levels of a bath atom. We note that at high temperatures $e^{\frac{\hbar\omega}{KT}}+1 \to 2$ and consequently the spectral density [or the noise strength governed by Eq. (4.14)] or D is largely reduced. In other words, because of thermal saturation of the two levels of the atoms of the spin bath, the system-bath coupling is suppressed as the right-hand side of Eq. (4.17) tends to vanish at high temperatures and consequently the decay rate is expected to be anomalous. In order to avoid this thermal saturation it is necessary to work below a saturation temperature T_s ($T_s = \hbar\omega_0/K$) so that temperatures are in the range $0 \leqslant T < T_s$. At low but finite temperatures, the right-hand side of expression (4.17) reduces to $\frac{\hbar\omega}{2}[1-2e^{-\hbar\omega/KT}]$. This implies relatively strong, effective system-bath coupling as the temperature is lowered well below the saturation temperature around which the rate is almost constant. This is shown in Fig. 2. Furthermore, it follows that all the quantities appearing in the square brackets inexpression (4.13) are positive and therefore the quantum factor due to nonlinear correction of the potential enhances the rate. This is also shown in Fig. 2 for several values of Δ.

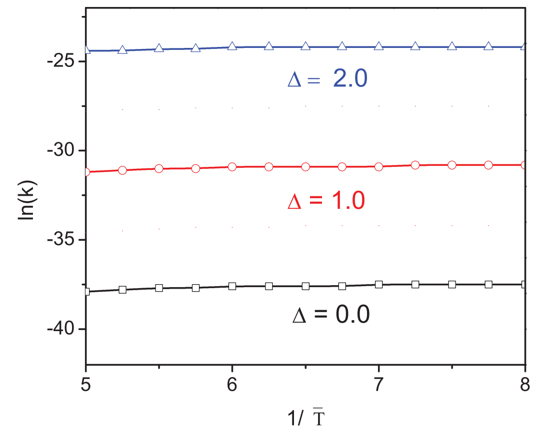

FIG. 2. (Color online) The variation of $\ln(k)$ vs inverse of scaled temperature $1/\bar{T}$ $\left(1/\bar{T} = \frac{\hbar\omega_0}{KT}\right)$ for quantum Smoluchowski rate constant k well below the saturation temperature. (Scale arbitrary.)

Summarizing the above discussions, we note that as the number of bath degrees of freedom approaches infinity, the effects of a spin bath are similar to those of a harmonic bath at zero temperature. The effective spectral density which contains a temperature-dependent factor plays a significant role in the diffusion coefficient D_f of the particle in a spin bath or the rate coefficient k. As the temperature rises there is an effective reduction of system-bath coupling due to thermal saturation. Thus the finite-temperature behavior of the spin bath is markedly different from that of the harmonic bath treated earlier by Ankerhold *et al.* and others [24,25] in the context of overdamped quantum dynamics. The origin of this difference may be traced to two factors: First, while the harmonic bath reaches the well-known classical macroscopic limit, the spin bath, in a strict sense, does not. Second, the possibilities of thermally induced excitation in a harmonic bath are far wider as compared to that for a spin bath, ensuring easy thermal saturation in the latter case. The present theoretical analysis may be probed experimentally by observing the decay of a suitable molecular system trapped in a sea of quantum dots which have served as "artificial" two-level atoms in various situations [26,27]. By suitably varying the system size one may obtain a distribution of frequencies for the dots for studies of quantum dissipation in a spin bath.

V. CONCLUSION

In this paper we have derived a quantum Smoluchowski equation for a spin bath of two-level atoms. The quantum nature of the dynamics manifests itself through the nonlinearity of the system potential and the character of the bath. The restricted options for thermal excitation of the bath degrees of freedom, since only one level of each atom can be excited, makes the spin bath conspicuously different from the bosonic one. We have shown that, in general, quantization has a significant effect on the decay of the metastable state due to quantum noise of the spin degrees of freedom. The rate constant is finite at 0 K and exhibits the predominance of coherent behavior at low but finite temperatures. At high temperatures equalization of population of both the levels leads to thermal saturation and suppression of system-bath coupling. The method is independent of path integral approaches and is classical in spirit from an application point of view. We hope that the present analysis will also be useful for several related issues in rate processes and transport in thermodynamically open systems.

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APPENDIX: THE CONDITION FOR QUANTUM OVERDAMPED MOTION IN A SPIN BATH—A DIMENSIONAL AND SCALING ANALYSIS

Equation (2.6) is a Langevin equation for the quantum mechanical mean position ($q = \langle \hat{q} \rangle$) of the particle and is classical looking in form. It involves quantum mechanical dispersion around this mean and the c-number noise of the spin bath. A closer scrutiny into the classically inspired treatment followed here in deriving a quantum Smoluchowski equation may be in order for identifying the appropriate parameter regime for its validity. Specifically, we need to address the following question: When is it valid to neglect the inertial term in Eq. (2.6)? To answer the question we carry out a dimensional and scaling analysis.

We begin with Eq. (2.6) and use expression (3.1) to obtain

$$\ddot{q} = -\gamma_0 \dot{q} - V'_{\text{quan}}(q, \langle \delta \hat{q}^n \rangle) + \eta(t). \tag{A1}$$

For convenience, we make the appearance of mass m explicit (m was set unity) and the coordinate dimensionless as $\tilde{q} = \frac{q}{\mathscr{Q}}$, where $\mathscr{Q}$ is a measure of a definite length scale appropriate for the problem. Equation (A1) then reads as

$$m\mathscr{Q}\frac{\partial^2 \tilde{q}}{\partial t^2} = -m\Gamma\mathscr{Q}\frac{\partial \tilde{q}}{\partial t} - \frac{\partial}{\partial \tilde{q}}\tilde{V}_{\text{quan}}(\tilde{q}) + \eta(t), \tag{A2}$$

where we have set $m\Gamma = \gamma_0$ and the potential is scaled as denoted by the tilde ($\sim$). As a next step we introduce a dimensionless time

$$\tau \equiv t/\mathscr{T}, \tag{A3}$$

where $\mathscr{T}$ is the characteristic time scale to be chosen later. For a "proper" choice of $\mathscr{T}$ the derivatives $\frac{d\tilde{q}}{d\tau}$ and $\frac{d^2\tilde{q}}{d\tau^2}$ should be of order unity, i.e., $O(1)$. Expressing $\dot{\tilde{q}} = \frac{1}{\mathscr{T}}\frac{d\tilde{q}}{d\tau}$ and $\ddot{\tilde{q}} = \frac{1}{\mathscr{T}^2}\frac{d^2\tilde{q}}{d\tau^2}$ we write (A2) as

$$\frac{m\mathscr{Q}}{\mathscr{T}^2}\frac{d^2\tilde{q}}{d\tau^2} = -\frac{m\Gamma\mathscr{Q}}{\mathscr{T}}\frac{d\tilde{q}}{d\tau} - \frac{\partial}{\partial\tilde{q}}\tilde{V}_{\text{quan}}(\tilde{q}) + \sqrt{\frac{m\Gamma}{\mathscr{T}}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}}\,\tilde{\eta}. \tag{A4}$$

In writing down the noise term of Eq. (A4) we have taken care of the correlation function of $\eta(t)$ which may be rewritten [Eq. (3.4)] as

$$\langle \eta(t)\eta(t')\rangle = \frac{m\Gamma}{\mathscr{T}}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\delta(\tau-\tau'), \tag{A5}$$

where the δ function in (A5) is dimensionless. Equation (A4) is now a force balance equation. Recognizing that $(\frac{m\Gamma}{\mathscr{T}}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT})^{\frac{1}{2}}$ has the dimension of force, (A4) can be nondimensionalized by dividing it with this quantity, so that we obtain

$$\begin{aligned}
&\frac{m\mathscr{Q}}{\mathscr{T}^2\left(\frac{m\Gamma}{\mathscr{T}}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\right)^{\frac{1}{2}}}\frac{d^2\tilde{q}}{d\tau^2}\\
&\quad= -\frac{(m\Gamma)^{\frac{1}{2}}\mathscr{Q}}{\left(\mathscr{T}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\right)^{\frac{1}{2}}}\frac{d\tilde{q}}{d\tau}\\
&\qquad-\left(\frac{m\Gamma}{\mathscr{T}}\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\right)^{-\frac{1}{2}}\frac{\partial\tilde{V}}{\partial\tilde{q}} + \tilde{\eta}.
\end{aligned} \tag{A6}$$

We are interested in a dynamical regime when the left-hand side of Eq. (A6) is negligible to all other terms. Then the "proper" choice of the scale of $\mathscr{T}$ implies that all the terms on the right-hand side are of $O(1)$, where the left-hand side is much less than unity. (Also note that $\langle \delta\hat{q}^n\rangle$ can be expressed in terms of mean motion q as shown in Sec. IV, in the potential term which does not involve the friction coefficient or temperature explicitly.) We thus require

$$\frac{\mathscr{Q}}{\sqrt{\mathscr{T}}}\left(\frac{m\Gamma}{\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}}\right)^{\frac{1}{2}} \approx O(1) \tag{A7}$$

and

$$\frac{m\mathscr{Q}}{\mathscr{T}^{3/2}\left(m\Gamma\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}\right)^{\frac{1}{2}}} \ll 1. \tag{A8}$$

The first condition sets the time scale $\mathscr{T}$ or the natural choice is

$$\mathscr{T} = \frac{m\Gamma\mathscr{Q}^2}{\left(\frac{\hbar\omega_0}{2}\right)\tanh\frac{\hbar\omega_0}{2KT}}. \tag{A9}$$

With (A9) the other condition becomes

$$\frac{\frac{\hbar\omega_0}{2}\tanh\frac{\hbar\omega_0}{2KT}}{m\Gamma^2\mathscr{Q}^2} \ll 1. \tag{A10}$$

Reverting back to the original notations, i.e., making mass and length scale unity ($m = \mathscr{Q} = 1$ so that $\gamma_0 = \Gamma$) the condition (A10) reads as

$$\frac{\hbar\omega_0}{2\gamma_0^2}\tanh\frac{\hbar\omega_0}{2KT} \ll 1. \tag{A11}$$

(A11) is the condition for quantum overdamped motion. This involves both the relevant frequency scales of the dissipative dynamics ω_0 and γ_0. The condition says that the inertial term in Eq. (2.6) is negligibly small in the Markovian limit (i.e., $\tau_c \to 0$), when $\frac{\omega_0}{\gamma_0^2}$ is small. The condition is also favored at low but finite temperatures (below a saturated temperature) and even at 0 K when the factor is unity. Otherwise the contribution to the damping will be vanishingly small. We mention in passing that this scaling and dimensional analysis [28] may also be applied to a quantum Smoluchowski equation for a harmonic bath for identifying an appropriate parameter regime for dissipative dynamics.

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