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Multilevel tunneling and coherence: Dissipative spin-hopping dynamics at finite temperatures

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The real-time dynamics of a quantum-mechanical particle in a dissipative double-well potential at finite temperatures is solved *ab initio* by means of a multisite spin-hopping analysis. Both the macroscopic-quantum-coherence and macroscopic-quantum-tunneling regimes are covered. The theory gives a unified picture of tunneling transport and vibrational relaxation. The analysis is based on the Ohmic-model Hamiltonian [A. O. Caldeira and A. J. Leggett, *Ann. Phys. (N.Y.)* **149**, 374 (1983); R. Zwanzig, *J. Stat. Phys.* **9**, 215 (1973)] or the equivalent “particle-on-a-string” model [H. Dekker, *Phys. Rev. A* **31**, 1067 (1985)]. The reduced quantum Liouville equation for the particle is derived and written in the energy representation. The usual truncation to the ground-state doublet of the vibrational ladder is *not* made. The *interdoublet* vibrational dynamics considerably simplifies upon coarse-graining and in the harmonic-well approximation. The *intradoublet* pseudospin dynamics is treated in the “noninteracting-blip approximation” [A. J. Leggett *et al.*, *Rev. Mod. Phys.* **59**, 1 (1987)]. The coarse-grained vibrational processes give rise to a Markovian one-step spin hopping between adjacent doublets (or sites). *Inter alia* “inhomogeneous broadening” and “motional narrowing” [P. E. Parris and R. Silbey, *J. Chem. Phys.* **83**, 5619 (1985)] are discussed as special cases.

I. INTRODUCTION

The motion of a particle in a double-well potential that is dissipatively coupled to a thermal environment can be considered as a prototype model for studying the behavior of metastable states [1], both classically [2–6] and quantum mechanically [7–11]. The dissipative double-well system is of considerable importance, not only theoretically but also from the point of view of current experiments. For instance, in modern solid-state physics it is a paradigm for macroscopic-quantum-coherent superposition [12,13] of magnetic flux states in experimental superconducting-quantum-interference devices [14,15]. In that case the “particle” coordinate is given by the total magnetic flux threading a superconducting ring containing a Josephson junction. Dissipative environmental effects arise, e.g., from external circuit loading [16] or from normal (Ohmic) state channels (phonons) in the junction’s oxide layer [17,18].

For the isolated system the Hamiltonian reads $H_0 = p^2/2m + U(x)$ and the energy spectrum follows from the elementary Schrödinger equation $(E - H_0)|n\rangle = 0$, where $n = 0, 1, \dots$ labels the eigenstates [19]. A typical double-well potential consists of two local minima at $x = \pm a$ (with harmonic frequency ω_0) which are separated by a barrier at $x = 0$ (with height $U_0 \gg \hbar\omega_0$). For a perfectly symmetric potential with an infinite barrier, the local potential wells would be noninteracting and the energy spectrum of the system would be double degenerate. Once the barrier becomes finite, this degeneracy will be lifted as a consequence of tunneling interactions between the localized states, and the spectrum becomes a ladder of vibrational doublets with energies $E_n \pm \frac{1}{2}\hbar\Delta_n$. By means of a WKB-type matching of

wave functions one finds [20] $\Delta_n = \bar{\omega}(A^n/n!)\exp(-B)$ with $\bar{\omega} = 2a\omega_0\sqrt{\omega_0/\pi\hbar}\exp(\omega_0\tau_0)$, $A = (\pi/2)(\bar{\omega}/\omega_0)^2$, $B = S_0/\hbar$, and τ_0 and S_0 the so-called “instanton” lifetime and action [21]. For instance, for the archetypical quartic potential one has $\omega_0\tau_0 = \ln 2$ and $S_0 = 16U_0/3\omega_0$, with $U_0 = \frac{1}{8}ma^2\omega_0^2$.

If at time $t = 0$ the particle is localized in one of the two wells such that the initial wave packet only involves the lowest-lying doublet (i.e., $n = 0$), then for the isolated system the probability of finding it in that particular well at some other time is $\sigma_0(t) = \cos\Delta_0 t$. However, this coherence is easily destroyed. For instance, the (doublet-splitting) spectrum is such [20] that upon squeezing the initial wave packet—so that it involves not only the local ground state but excited states as well—the oscillation will be quickly destroyed through pure dephasing (“homogeneous broadening”). Adding an asymmetry to the potential also strongly suppresses the oscillation’s amplitude [22]. Moreover, destruction of quantum coherence will generally be significant if the interesting degree of freedom (e.g., the circulating supercurrent supporting the flux in the Josephson ring) is coupled to a heat bath.

The influence of a dissipative thermal environment on the loss of macroscopic quantum coherence [12,13] has given rise to considerable recent research activity [1,7–11,22]. The investigations typically involve only the ground-state doublet of a (nearly) symmetric double-well potential. This dissipative two-level system appropriately goes by the name of “spin-boson” model. The most thoroughly studied case is that of an Ohmic spectral density for the system-bath coupling (which is equivalent to a “particle-on-a-string” model [16,23–25]). The ensuing frictional renormalization of the “bare” tunneling matrix

element (i.e., Δ_0) not only strongly suppresses the quantum oscillations between the two wells, but at zero temperature even strictly prohibits any tunneling transport whenever the coupling is sufficiently strong. The relevant parameter is $\alpha = 4\lambda a^2 / \pi \hbar$ (where 2λ is the classical friction coefficient), and the localization criterion is $\alpha > 1$. Since $\alpha \approx (\lambda/\omega_0)(S_0/\hbar)$, this strong quantum friction condition can be satisfied even for rather weak classical damping.

The reduction of the double-well system to the two-level subspace is *inter alia* valid only if [26,27] both $2\pi\alpha k_B T / \hbar\omega_0 \rightarrow 0$ and $24(S_0/\hbar)\exp(-\hbar\omega_0/2k_B T) \rightarrow 0$ (the numerical value of the prefactor is specific to the quartic potential). With the typical experimental values $\alpha \approx 1$, $S_0/\hbar \approx 20$, and $6 \lesssim \hbar\omega_0/k_B T \lesssim 18$, the two-level conditions are by no means obviously satisfied. Unfortunately, an earlier attempt at a real-time description of the system's quantum dynamics without making the two-level approximation ended in a mathematical deadlock: for the quartic barrier the path integral for the fully reduced density operator involves Airy functions that preclude further analysis [28]. Next, a significant contribution was made by Parris and Silbey [29]. In fact, from our present point of view they wrote the only comparable paper. However, the present *ab initio* unified treatment of both the vibrational relaxation and the dissipative spin dynamics substantially differs from that of Ref. [29]. In addition, a discussion of the *asymmetric* potential will be included here.

In the present paper the double-well potential model will be discussed (i) *including* Ohmic coupling to a dissipative thermal environment, but (ii) *without* making the two-state approximation. In Sec. II the model Hamiltonian following Zwanzig-Caldeira-Leggett [17,30] for the dissipative double-well system is introduced as the explicit starting point for the analysis. A reduced density-operator equation for the particle is obtained by partially eliminating the bath dynamics. In Sec. III this equation is written in the local-energy representation, which allows for a further evaluation of the vibrational relaxation. Coarse-graining (on a time scale ω_0^{-1}) considerably simplifies the equations of motion. The remaining dynamics still involves both *interdoublet* and *intradoublet* processes. The former give rise to Markov-type spin hopping. The latter spin dynamics is considered in Sec. IV, introducing appropriate adaptations of the “displaced-bath-oscillator representation” [7,10,11,31] and “noninteracting-blip approximation” [8,10,11]. The biased potential is discussed in Sec. V. Some concluding remarks are given in Sec. VI while the Appendix contains an analysis of the vibrational quantum diffusion coefficients. An exhaustive account of the theory is available upon request [32].

II. THE MODEL

The Hamiltonian of a particle (of unit mass, for convenience) that moves along a coordinate x under the influence of a force arising from a potential $U(x)$ and is bilinearly coupled to an environment of harmonic oscillators may be given as [1,10,17,27,30]

$$H = \frac{1}{2}p^2 + U(x) + \frac{1}{2} \sum_k (p_k^2 + \omega_k^2 x_k^2) + x \sum_k c_k x_k + \frac{1}{2} x^2 \sum_k c_k^2 / \omega_k^2. \quad (2.1)$$

The last term in (2.1) occurs more naturally in a particle-on-a-string model [24]. It cancels an infinite dissipative renormalization of the potential $U(x)$. The model is completed by specifying the spectral density

$$J(\omega) = \frac{\pi}{2} \sum_k (c_k^2 / \omega_k) \delta(\omega - \omega_k). \quad (2.2)$$

For Ohmic dissipation $J(\omega) = 2\lambda\omega f(\omega/\omega_c)$, where $f(\omega/\omega_c)$ is a cutoff function. The model of Ref. [24], e.g., yields $f = 1/(1 + \omega^2\tau_c^2)$. The time-dependent total-density operator

$$\rho_t = e^{-(i/\hbar)Ht} \rho(0) e^{(i/\hbar)Ht} \quad (2.3)$$

obeys the Liouville equation $\dot{\rho}_t = -(i/\hbar)[H, \rho_t]$. Using the Hamiltonian (2.1) one obtains

$$\begin{aligned} \dot{\rho}_t = & -\frac{i}{\hbar}[H_0, \rho_t] - \frac{i}{\hbar} \sum_k c_k [xx_k, \rho_t] \\ & - \frac{i}{2\hbar} \sum_k (c_k / \omega_k)^2 [x^2, \rho_t] - \frac{i}{\hbar} [H_B, \rho_t], \end{aligned} \quad (2.4)$$

where $H_0 = \frac{1}{2}p^2 + U(x)$ and H_B represents the free-bath Hamiltonian. Now let (2.4) be used only for averaging functions $f(x, p)$ which do not explicitly depend on the x_k and p_k . This restriction allows (2.4) to be written in the form of a (quantum-mechanical) continuity equation [16] for the *particle* only. Namely, for an arbitrary function $f(x, p)$ one has the identity $\text{Tr}([xx_k, \rho_t]f) = \frac{1}{2}\text{Tr}([x, [x_k, \rho_t]_+]f)$ since always $[x, x_k] = 0$ and $[p, x_k] = 0$. The subscript “plus” denotes anticommutation. Since $[x, f] = i\hbar \partial f / \partial p$, the right-hand side of this identity is in the desired form. For the “counterterm” in (2.4) one similarly has the identity $\text{Tr}([x^2, \rho_t]f) = \text{Tr}([x, [x, \rho_t]_+]f)$. Again, the right-hand side is in the Liouville form. By means of these two identities (2.4) may be rewritten as

$$\begin{aligned} \dot{\rho}_t = & -\frac{i}{\hbar}[H_0, \rho_t] - \frac{i}{2\hbar} \sum_k c_k [x, [x_k + c_k x / \omega_k^2, \rho_t]_+] \\ & - \frac{i}{\hbar} [H_B, \rho_t]. \end{aligned} \quad (2.5)$$

Let us now eliminate the actual bath response. Note that the operators x and x_k in (2.5) are at $t=0$. Therefore, integrate the environmental equations of motion $\dot{x}_k = p_k$ and $\dot{p}_k = -\omega_k^2 x_k - c_k x$ from $t = -\infty$ to $t=0$. This yields [11,32] the (dynamical) transformation

$$x_k = x_k^{(0)} - (c_k / \omega_k^2) \left[x - \int_{-\infty}^0 \cos \omega_k(t-t') p(t') dt' \right], \quad (2.6)$$

where $x_k^{(0)} = \sqrt{\hbar/2\omega_k}(a_k + a_k^*)$ is the free-bath operator at $t=0$. Substituting (2.6) for x_k into (2.5) and using (2.2) for the Ohmic case (with $\omega_c \rightarrow \infty$), one obtains

$$\begin{aligned} \dot{\rho}_t = & -\frac{i}{\hbar}[H_0, \rho_t] - \frac{i}{2\hbar}[x, [2\lambda p + \mathcal{F}(0), \rho_t]_+] \\ & - \frac{i}{\hbar}[H_B, \rho_t] , \end{aligned} \quad (2.7)$$

where $\mathcal{F}(0) = -\sum_k c_k x_k^{(0)}$. Finally, the last term in (2.6) is eliminated by defining

$$\rho = e^{(i/\hbar)H_B t} \rho_t e^{-(i/\hbar)H_B t} . \quad (2.8)$$

The resulting quantum Liouville equation for ρ reads

$$\dot{\rho} = -\frac{i}{\hbar}[H_0, \rho] - \frac{i}{\hbar}\lambda[x, [p, \rho]_+] - \frac{i}{2\hbar}[x, [\mathcal{F}(t), \rho]_+] , \quad (2.9)$$

where

$$\mathcal{F}(t) = -\sum_k c_k x_k^{(0)}(t) , \quad (2.10)$$

with

$$x_k^{(0)}(t) = \left[\frac{\hbar}{2\omega_k} \right]^{1/2} (a_k e^{-i\omega_k t} + a_k^* e^{i\omega_k t}) . \quad (2.11)$$

The $x_k^{(0)}(t)$ represent the free-bath dynamics and $\mathcal{F}(t)$ is an *operator-valued* noise source. In Ref. [32] it is shown that (2.9) is exactly equivalent to the particle's (operator) quantum Langevin equation. Using the standard properties [16,24,33]

$$\begin{aligned} \langle a_k \rangle &= 0 , \quad \langle a_k a_l \rangle = 0 , \quad \langle a_k^* a_l \rangle = N_k \delta_{kl} , \\ N_k &= 1 / [\exp(\beta \hbar \omega_k) - 1] , \quad \beta = 1 / k_B T , \end{aligned} \quad (2.12)$$

of a bosonic environment at temperature T , one finds

$$\begin{aligned} \langle \mathcal{F}(t) \rangle &= 0 , \\ \langle \{ \mathcal{F}(t) \mathcal{F}(0) \} \rangle &= \frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \coth(\tfrac{1}{2}\beta \hbar \omega) \cos \omega t , \end{aligned} \quad (2.13)$$

where the curly brackets indicate symmetrization. If $\hbar \rightarrow 0$, the Ohmic case leads to the classical result $\langle \mathcal{F}(t) \mathcal{F}(0) \rangle = 4\lambda k_B T$.

III. VIBRATIONAL RELAXATION

A. The spectrum

Let us now apply the general Ohmic equation (2.9) to the double-well problem. Throughout it will be assumed that the barrier is high, i.e., $U_0 \gg \max(\hbar \omega_0, k_B T)$. The spectrum of H_0 consists of a ladder of vibrational doublets. Let the eigenstates of H_0 be $|n\rangle$, with $n=0,1,\dots$. The n th doublet is formed by the states $|2n\rangle$ and $|2n+1\rangle$. The associated energy values are defined through

$$\begin{aligned} H_0 |2n\rangle &= (E_n - \tfrac{1}{2}\hbar \Delta_n) |2n\rangle , \\ H_0 |2n+1\rangle &= (E_n + \tfrac{1}{2}\hbar \Delta_n) |2n+1\rangle , \end{aligned} \quad (3.1)$$

so that $\hbar \Delta_n$ represents the energy splitting within the n th doublet. The (global) particle states form a complete and orthonormal set, i.e., $\langle n|m \rangle = \delta_{nm}$ and $\sum_n |n\rangle \langle n| = 1$.

They have alternately even or odd parity, beginning with the even ground state $|0\rangle$. In particular, the lower-lying states are easily depicted as symmetric or antisymmetric linear combinations of highly *localized* states (near the potential minima). It will therefore be convenient to define localized states $|\pm n\rangle$ as

$$|\pm n\rangle = 2^{-1/2} (|2n\rangle \pm |2n+1\rangle) . \quad (3.2)$$

Using (3.1) and (3.2) one finds

$$H_0 |\pm n\rangle = E_n |\pm n\rangle - \tfrac{1}{2}\hbar \Delta_n |\mp n\rangle . \quad (3.3)$$

The $|\pm n\rangle$ also form a complete orthonormal set, i.e., $\langle \pm n | \pm m \rangle = \delta_{\pm n, \pm m}$ and $\sum_n |\pm n\rangle \langle \pm n| = 1$. Let us now take local-state matrix elements of (2.9). For instance, for the "free" particle one obtains

$$\begin{aligned} \dot{\rho}_{\pm n, \pm m}^{(0)} &= -\frac{i}{\hbar} \langle \pm n | [H_0, \rho] | \pm m \rangle \\ &= -i\omega_{nm} \rho_{\pm n, \pm m} + \tfrac{1}{2}i\Delta_n \rho_{\mp n, \pm m} - \tfrac{1}{2}i\Delta_m \rho_{\pm n, \mp m} , \end{aligned} \quad (3.4)$$

where $\rho_{\pm n, \pm m} = \langle \pm n | \rho | \pm m \rangle$ and $\omega_{nm} = (E_n - E_m)/\hbar$. In what follows the density matrix will be coarse-grained on a time scale of many vibrational periods (*first approximation*). As an immediate consequence the rapidly oscillating (with frequencies $\omega_{nm} \neq 0$) elements $\rho_{\pm n, \pm m}$ with $n \neq m$ average to zero.

B. The dissipation terms

To evaluate the friction terms

$$\dot{\rho}_{\pm n, \pm n}^{(1)} = -\frac{i}{\hbar} \lambda \langle \pm n | [x, [p, \rho]_+] | \pm n \rangle , \quad (3.5)$$

it will be useful to define local coordinates ξ by $x|\pm n\rangle = (\pm a + \xi)|\pm n\rangle$, and to separately consider local (i.e., diagonal $\rho_{+n, +n}$ and $\rho_{-n, -n}$) and global (i.e., antidiagonal $\rho_{+n, -n}$ and $\rho_{-n, +n}$) contributions. Upon inserting two resolutions of unity and disregarding all density-matrix elements with $n \neq m$, one first of all finds

$$\begin{aligned} \dot{\rho}_{+n, +n}^{(1)} &= \lambda \rho_{+n, +n} - \frac{i}{\hbar} \lambda \sum_m (\xi_{+n, +m} \rho_{+m, +n} \\ &\quad - \rho_{+n, +m} \xi_{+m, +n}) \rho_{+m, +m} , \end{aligned} \quad (3.6)$$

where all matrix elements have been evaluated strictly locally such that $\rho_{+n, -m} = \xi_{+n, -m} = 0$. The corresponding result for $\rho_{-n, -n}$ follows from (3.6) by a change of sign in all indices. Let us now evaluate the local $\rho_{+n, +m}$ and $\xi_{+n, +m}$ by taking the potential minima to be perfectly harmonic (*second approximation*). This yields

$$\begin{aligned} \dot{\rho}_{+n, +n}^{(1)} &= \lambda [(n+1) \rho_{+(n+1), +(n+1)} + \rho_{+n, +n} \\ &\quad - n \rho_{+(n-1), +(n-1)}] . \end{aligned} \quad (3.7)$$

For the dynamics of $\rho_{+n, -n}$ a strictly local evaluation is insufficient (e.g., to ensure relaxation to global equilibrium). Namely, in that case a global term proportional to

$\alpha p_{+n,-n}(\rho_{+n,+n} + \rho_{-n,-n})$ shows up on the right-hand side of (3.5). Invoking $p = (-i/\hbar)[x, H_0]$ and using (3.3) to calculate $p_{+n,-n}$ then yields

$$\begin{aligned} \dot{\rho}_{+n,-n}^{(1)} &= \frac{1}{2}\pi\alpha\Delta_n(\rho_{+n,+n} + \rho_{-n,-n}) \\ &+ \lambda[(n+1)\rho_{+(n+1),-(n+1)} + \rho_{+n,-n} \\ &- n\rho_{+(n-1),-(n-1)}], \end{aligned} \quad (3.8)$$

where $\alpha = 4\lambda a^2/\pi\hbar$ is the quantum friction coefficient [10,22]. The corresponding result for $\rho_{-n,+n}$ follows from (3.8) by a sign change in all indices.

C. The fluctuations

The last contribution from (2.9) immediately leads to

$$\dot{\rho}_{+n,+n}^{(2)} = -\frac{i}{\hbar}a[\mathcal{F}(t), \rho_{+n,+n}] - \frac{i}{\hbar}\langle +n | [\xi\mathcal{F}(t), \rho] | +n \rangle. \quad (3.9)$$

The first term on the right-hand side of (3.9) pertains to the global transport and will be further dealt with in Sec. IV. The second term describes transitions in the local oscillator system. Since the harmonic-oscillator [16,24,32,34–36] correlations always buildup on a very short time scale of the order of $\omega_0^{-1} \ll \Delta_n^{-1}$, it will be possible to evaluate the local fluctuations independent of the global transport. In that case the averaging over the thermal reservoir (2.12) can be done exactly (i.e., for all values of friction and temperature). The result reads

$$\dot{\rho}_{+n,+n}^{(2)} = \sum_m W_{nm}\rho_{+m,+m} - \frac{i}{\hbar}a[\mathcal{F}(t), \rho_{+n,+n}], \quad (3.10)$$

where the W matrix induces a Markovian random walk on the vibrational ladder. Its only nonzero elements are

$$\begin{aligned} W_{n,n+1} &= (n+1)(\lambda + D_{pp}/\hbar\omega_0), \\ W_{n,n} &= \lambda - (2n+1)D_{pp}/\hbar\omega_0, \\ W_{n,n-1} &= -n(\lambda - D_{pp}/\hbar\omega_0), \end{aligned} \quad (3.11)$$

where in view of coarse-graining the quantum diffusion coefficient $D_{pp}(t)$ has been replaced by its value $D_{pp} = D_{pp}(\infty)$ as given in (A9). The coefficient D_{px} does not contribute to the secular dynamics [32], while D_{xx} is strictly zero. The corresponding birth and death rates [5] read $r_n^{(+)} = -(n+1)(\lambda - D_{pp}/\hbar\omega_0)$ and $r_n^{(-)} = n(\lambda + D_{pp}/\hbar\omega_0)$, such that $W_{n \neq m} = r_m^{(-)}\delta_{n,m-1} + r_m^{(+)}\delta_{n,m+1}$. Similarly one obtains

$$\dot{\rho}_{+n,-n}^{(2)} = \sum_m W_{nm}\rho_{+m,-m} - \frac{i}{\hbar}a[\mathcal{F}(t), \rho_{+n,-n}]_+. \quad (3.12)$$

Collecting the various contributions for $\dot{\rho}^{(0)}$, $\dot{\rho}^{(1)}$, and $\dot{\rho}^{(2)}$ finally yields

$$\begin{aligned} \dot{\rho}_{+n,+n} &= -\frac{1}{2}i\Delta_n(\rho_{+n,-n} - \rho_{-n,+n}) + \sum_m W_{nm}\rho_{+m,+m} \\ &+ \frac{i}{\hbar}a[\rho_{+n,+n}\mathcal{F}(t) - \mathcal{F}(t)\rho_{+n,+n}], \end{aligned} \quad (3.13)$$

and

$$\begin{aligned} \dot{\rho}_{+n,-n} &= -\frac{1}{2}i\Delta_n(\rho_{+n,+n} - \rho_{-n,-n}) + \frac{1}{2}\pi\alpha\Delta_n p_n \\ &+ \sum_m W_{nm}\rho_{+m,-m} \\ &- \frac{i}{\hbar}a[\rho_{+n,-n}\mathcal{F}(t) + \mathcal{F}(t)\rho_{+n,-n}], \end{aligned} \quad (3.14)$$

where $p_n = \rho_{+n,+n} + \rho_{-n,-n}$ is the total probability of finding the system in the n th energy doublet. The results for $\dot{\rho}_{-n,-n}$ and $\dot{\rho}_{-n,+n}$ follow by (i) changing sign in all indices of the density matrix elements and (ii) in addition letting $a \rightarrow -a$ in the (global) noise term.

Defining

$$\begin{aligned} \rho_{+n,+n} &= \frac{1}{2}(p_n + \sigma_n), \\ \rho_{-n,-n} &= \frac{1}{2}(p_n - \sigma_n), \\ \rho_{+n,-n} &= \frac{1}{2}(\varepsilon_n - i\delta_n), \end{aligned}$$

and

$$\rho_{-n,+n} = \frac{1}{2}(\varepsilon_n + i\delta_n),$$

one may rewrite (3.13) and (3.14) as

$$\begin{aligned} \dot{p}_n &= \sum_m W_{nm}p_m, \\ \dot{\sigma}_n &= -\Delta_n\delta_n + \sum_m W_{nm}\sigma_m, \\ \dot{\varepsilon}_n &= \sum_m W_{nm}\varepsilon_m + \pi\alpha\Delta_n p_n - \frac{a}{\hbar}[\delta_n\mathcal{F}(t) + \mathcal{F}(t)\delta_n], \\ \dot{\delta}_n &= \Delta_n\sigma_n + \sum_m W_{nm}\delta_m + \frac{a}{\hbar}[\varepsilon_n\mathcal{F}(t) + \mathcal{F}(t)\varepsilon_n]. \end{aligned} \quad (3.15)$$

If $W_{nm} = 0$ (i.e., for a single doublet) the pseudospin form (3.15) is close to but not exactly that of the usual Heisenberg equations of motion for the (Pauli) spin-boson model [10,22]. Presently $\mathcal{F}(t)$ is given by the free rather than the interacting environment, while an explicit bath response term occurs in the equation for the energy ε_n . However, it can be shown that the usual spin-boson Heisenberg equations can be written in the single-doublet form of (3.15) rigorously [32].

IV. SPIN DYNAMICS

A. Displaced bath oscillators

Let us now implement appropriately adapted versions of the “displaced-bath-oscillator basis” and “noninteracting-blip approximation” [7–11,31]. For the single-spin-boson model the displaced-bath-oscillator basis diagonalizes the environmental part of the Hamiltonian, including the explicit interaction term with the spin. As a consequence the x and y components of the spin become “dressed” with bath operators. However, the z component is not affected. The unitary operator U , which has essentially the same effects on our pseudospin operators, is given by $U = \exp[-iXB(t)]$, where the global position operator

$$X = \sum_n (|+n\rangle\langle +n| - |-n\rangle\langle -n|)$$

is such that $X = -1$ (respectively, $X = +1$) on the left-hand (respectively, right-hand) side of the barrier, and where

$$\mathcal{B}(t) = \sum_k \mathcal{B}_k p_k^{(0)}(t), \quad (4.1)$$

with $\mathcal{B}_k = ac_k / 2\hbar\omega_k^2$ and $p_k^{(0)}(t) = \dot{x}_k^{(0)}(t)$. The operator U transforms the density operator ρ into ρ' according to $\rho' = U\rho U^*$, so that

$$\begin{aligned} \rho'_{+n,+n} &= e^{-i\mathcal{B}(t)} \rho_{+n,+n} e^{+i\mathcal{B}(t)}, \\ \rho'_{+n,-n} &= e^{-i\mathcal{B}(t)} \rho_{+n,-n} e^{-i\mathcal{B}(t)}. \end{aligned} \quad (4.2)$$

Notice that upon taking bath averages $\langle p'_n(t) \rangle = \langle p_n(t) \rangle$ and $\langle \sigma'_n(t) \rangle = \langle \sigma_n(t) \rangle$. In the new basis (3.14) becomes

$$\begin{aligned} \dot{\rho}'_{+n,-n} &= -\frac{1}{2}i\Delta_n(e^{-2i\mathcal{B}(t)}\rho'_{+n,+n} - \rho'_{-n,-n}e^{-2i\mathcal{B}(t)}) \\ &\quad + \frac{1}{2}\pi\alpha\Delta_n e^{-i\mathcal{B}(t)}p_n e^{-i\mathcal{B}(t)} + \sum_m W_{nm}\rho'_{+m,-m}, \end{aligned} \quad (4.3)$$

where use has been made of the free-bath Hamiltonian and (2.10) for $\mathcal{F}(t)$ to determine the time derivative of $\exp[\pm i\mathcal{B}(t)]$. Now let the Green's function $p_n(t) = G_{nm}(t)$ of the vibrational c -number random walk (3.15) be known. Then formally integrating (4.3) yields

$$\begin{aligned} \rho'_{+n,-n}(t) &= \sum_m G_{nm}(t)\rho_{+m,-m}(0) + \frac{1}{2}\int_0^t \sum_m \Delta_m G_{nm}(t-t') \{ \pi\alpha e^{-i\mathcal{B}(t')} p_m(t') e^{-i\mathcal{B}(t')} \\ &\quad - i[e^{-2i\mathcal{B}(t')}\rho'_{+m,+m}(t') - \rho'_{-m,-m}(t')e^{-2i\mathcal{B}(t')}] \} dt'. \end{aligned} \quad (4.4)$$

Substituting (4.4) for $\rho'_{+n,-n}(t)$ into the formal solution for $\rho'_{+n,+n}(t)$ as arising from (3.13), one obtains

$$\begin{aligned} \rho'_{+n,+n}(t) &= \sum_m G_{nm}(t)\rho_{+m,+m}(0) \\ &\quad - \frac{1}{4}\int_0^t dt' \int_0^{t'} dt'' \sum_m \Delta_m G_{nm}(t-t') \\ &\quad \times \sum_l \Delta_l G_{ml}(t'-t'') e^{-i\mathcal{B}(t)} \{ e^{i\mathcal{B}(t')} [ie^{-i\mathcal{B}(t'')} \pi\alpha p_l(t'') e^{-i\mathcal{B}(t'')} - e^{-2i\mathcal{B}(t'')} \rho'_{-l,-l}(t'')] \\ &\quad + \rho'_{+l,+l}(t'') e^{-2i\mathcal{B}(t'')}] e^{i\mathcal{B}(t')} + \text{H.c.} \} e^{i\mathcal{B}(t)}, \end{aligned} \quad (4.5)$$

where we have taken the particle to be initially localized at $x = \pm a$ so that $\rho'_{+n,-n}(0) = 0$, as usual, and where H.c. stands for “Hermitian conjugate.” Noticing that $a \rightarrow -a$ implies $\mathcal{B}(t) \rightarrow -\mathcal{B}(t)$ in view of (4.1), the corresponding result for $\rho'_{-n,-n}(t)$ follows as before.

B. Multisite noninteracting blips

Let us now evaluate (4.5) in the so-called noninteracting-blip approximation. The terminology stems from the pertinent set of trajectories in the path-integral treatment given in Ref. [10]. Here we follow the analysis of Ref. [11], where it has been shown how exactly the same results are obtained by second-order perturbation theory in terms of the free-bath dressed tunneling operators $\Delta_n(t) = \Delta_n \exp[\pm 2i\mathcal{B}(t)]$. However, unlike Ref.

[11] the present analysis does not use spin-operator algebra. As extensively discussed in Ref. [10], the approximation is justified for both weak ($\alpha \lesssim \frac{1}{2}$) and strong quantum friction ($\alpha \gtrsim 1$). In the latter regime it holds good because the dressing drastically decreases (renormalizes) the tunneling frequencies.

The right-hand side of (4.5) is already of second order in the free-bath dressed tunneling elements (so that from here on the actual bath response term $\pi\alpha p_l$ will be dropped). Hence, upon taking environmental traces in the sense of (2.12), the spin and bath variables in the integrals now completely decouple. Noticing that $\langle \rho'_{+n,+n} \rangle = \langle \rho_{+n,+n} \rangle$, using the cyclic trace property for the bath averages and invoking the Baker-Hausdorff theorem $e^A e^B = \exp(A+B+i\mathcal{D}/2)$ if $[A,B] = i\mathcal{D}$ is a c -number, one finds

$$\begin{aligned} \rho_{+n,+n}^{(t)} &= \sum_m G_{nm}(t)\rho_{+m,+m}(0) + \frac{1}{2}\int_0^t dt' \int_0^{t'} dt'' \sum_m \Delta_m G_{nm}(t-t') \sum_l \Delta_l G_{ml}(t'-t'') \\ &\quad \times \langle \cos 2[\mathcal{B}(t') - \mathcal{B}(t'')] \rangle \cos \mathcal{D}(t'-t'') \sigma_l(t''), \end{aligned} \quad (4.6)$$

where for convenience the brackets on the “spin” variables have been dropped again and $i\vartheta(t'-t'')=2[\mathcal{B}(t'),\mathcal{B}(t'')]$. Using (4.1) and (2.2) yields

$$\vartheta(t)=\frac{4a^2}{\pi\hbar}\int_0^\infty d\omega \sin(\omega t)J(\omega)/\omega^2. \quad (4.7)$$

The remaining environmental averages are most easily calculated by means of the cumulant expansion [5,11]. Since the free bath is Gaussian with zero mean, only the second cumulant $2\gamma(t'-t'')$ contributes. It reads

$$\gamma(t)=\frac{4a^2}{\pi\hbar}\int_0^\infty d\omega [1-\cos(\omega t)]\coth(\frac{1}{2}\beta\hbar\omega)J(\omega)/\omega^2. \quad (4.8)$$

Adding the result for $\rho_{+,n,+n}(t)$ and $\rho_{-,n,-n}(t)$ one then immediately obtains

$$p_n(t)=\sum_m G_{nm}(t)p_m(0), \quad (4.9)$$

which shows the internal consistency of the analysis. On the other hand, subtraction yields

$$\sigma_n(t)=\sum_m G_{nm}(t)\sigma_m(0)-\int_0^t dt' \int_0^{t'} dt'' \sum_m \Delta_m G_{nm}(t-t') \sum_l \Delta_l G_{ml}(t'-t'') \cos\vartheta(t'-t'') e^{-\gamma(t'-t'')} \sigma_l(t''), \quad (4.10)$$

which is the multidoublet-hopping generalization of the standard result [10,11]. Taking $J(\omega)=2\lambda\omega \exp(-\omega/\omega_c)$, one obtains $\vartheta(t)=2\alpha \arctan(\omega_c t)$ from (4.7) while (4.8) yields

$$\gamma(t)=\alpha \ln(1+\omega_c^2 t^2)+2\alpha \ln[(\beta\hbar/\pi t)\sinh(\pi t/\beta\hbar)].$$

If $G_{nm}(t)=\delta_{nm}$ —i.e., for a single doublet—the solution (4.10) reduces *exactly* to the path-integral solution for the spin-boson model in the noninteracting-blip approximation [10,11]. The approximation has been shown [10] to be rigorous if $\alpha=\frac{1}{2}$ (for all T) and in the limit $\alpha k_B T/\hbar\Delta_{\text{ren}} \gg 1$, where $\Delta_{\text{ren}}=\Delta_n(\Delta_n/\omega_c)^{\alpha/(1-\alpha)}$ is the renormalized tunneling frequency. It also yields excellent results at $T=0$ if $\alpha \lesssim \frac{1}{2}$.

C. Special cases

In the limit of zero vibrational relaxation [i.e., $W=0$, or $|W_{lm}| \ll \Delta_n$, so that $G_{nm}(t)=\delta_{nm}$] the coherent oscil-

lations in the various “spin” polarizations $\sigma_n(t)$ will quickly dephase due to the (quasi-Weierstrass) distribution of the Δ_n [20]. This is the earlier-mentioned case of “inhomogeneous broadening.” On the other hand, if the local relaxation is much faster than the global transport one may set $G_{nm}(t)=p_n^e$. For the random walk (3.11) the stationary distribution $p_n^e=p_n(\infty)$ may be written as

$$p_n^e=Z^{-1}\exp(-\beta\mathcal{E}_n), \quad (4.11)$$

with

$$\mathcal{E}_n=(n+\frac{1}{2})\hbar\omega_{\text{eff}}$$

and

$$\omega_{\text{eff}}=(2/\hbar\beta)\text{arccoth}(D_{pp}/\lambda\hbar\omega_0),$$

so that $Z^{-1}=2\sinh(\frac{1}{2}\beta\hbar\omega_{\text{eff}})$. In this case (4.10) reduces to

$$\sigma_n(t)=p_n^e \left[X(0)-\int_0^t dt' \int_0^{t'} dt'' \sum_m (\Delta_m/\bar{\Delta}) \bar{f}(t'-t'') \sigma_m(t'') \right], \quad (4.12)$$

where $\bar{\Delta}=\sum_n p_n^e \Delta_n$, $X(t)=\sum_n \sigma_n(t)$, and $\bar{f}(t)=\bar{\Delta}^2 \cos\vartheta(t) e^{-\gamma(t)}$. Writing $\sigma_n(t)=p_n^e X(t)$ and once differentiating (4.12) with respect to time, one obtains

$$\dot{X}(t)+\int_0^t dt' \bar{f}(t-t') X(t')=0, \quad (4.13)$$

which is the usual form of the single-site dynamics

[10,11] except for the replacement of Δ_n by $\bar{\Delta}$. That is, the pseudospin’s migration on the energy “lattice” may suppress the inhomogeneous broadening and effectively improve the coherence of the spin dynamics, an effect called “motional narrowing” [29]. For instance, at zero temperature $X(t)$ can now be represented by the Mittag-Leffler function [37]. For $\alpha < \frac{1}{2}$ this function consists of a

“coherent” and “incoherent” part. For $\alpha \ll \frac{1}{2}$ the coherent part $X(t) = (1-\alpha)^{-1} e^{-\gamma t} \cos \Omega t$ — where $\Omega = \bar{\Delta}_{\text{eff}} \cos[\pi\alpha/2(1-\alpha)]$, $\gamma = \bar{\Delta}_{\text{eff}} \sin[\pi\alpha/2(1-\alpha)]$ and $\bar{\Delta}_{\text{eff}} = [\Gamma(1-2\alpha) \cos \pi\alpha]^{1/2(1-\alpha)} \bar{\Delta}_{\text{ren}}$ — dominates.

If $\frac{1}{2} < \alpha < 1$, the Mittag-Leffler function decays to zero in a purely algebraic fashion on the time scale $\bar{\Delta}_{\text{ren}}^{-1}$. If $\alpha > 1$, one has $X(t) = X(0)$. This is the dissipative freezing (or localization) phenomenon in the strong-quantum-damping regime [7–10,26]. An explicit calculation of $\bar{\Delta}$ is given in Ref. [32], where one may also find a discussion of the so-called “duplex” (or double-doublet [29]) system.

V. THE BIASED CASE

Let us now generalize the theory to include an asymmetry ϵ in the potential $U(x)$, which amounts to placing the “spin” in a (weak i.e., $\epsilon \ll \hbar\omega_0$) external field. This is easily achieved [26,27] by the addition of a linear term $(\epsilon/2a)x$, where the bias choice $U(\pm a) = \pm \epsilon/2$ is follow-

ing conventional spin-boson theory [10,22]. As a consequence the free-particle equation (3.4) will be modified. In particular, in the omnipresent secular local harmonic approximation one has

$$\dot{\rho}_{+n,-n}^{(0)} = -\frac{1}{2}i\Delta_n(\rho_{+n,+n} - \rho_{-n,-n}) - i(\epsilon/\hbar)\rho_{+n,-n}, \quad (5.1)$$

and similarly for its complex conjugate $\dot{\rho}_{-n,+n}^{(0)}$, while the results for $\dot{\rho}_{+n,+n}^{(0)}$ and $\dot{\rho}_{-n,-n}^{(0)}$ remain unchanged. Both the dissipative terms (3.7) and (3.8) and the fluctuation terms (3.10)–(3.12) are unaltered in the presence of a nonzero bias. Hence, only (3.14) acquires a bias term on its right-hand side. Alternatively, in the equations of motion (3.15) for ϵ_n and δ_n a term $-(\epsilon/\hbar)\delta_n$, respectively $+(\epsilon/\hbar)\epsilon_n$, must be added.

In the displaced oscillators basis (4.3) now involves a term $-i(\epsilon/\hbar)\rho'_{+n,-n}$. Hence, the pertinent generalization of (4.4) becomes

$$\rho'_{+n,-n}(t) = \sum_m G_{nm}(t) \rho_{+m,-m}(0) - \frac{1}{2}i \int_0^t \sum_m \Delta_m G_{nm}(t-t') e^{-i\epsilon(t-t')/\hbar} [e^{-2i\mathcal{B}(t')} \rho'_{+m,+m}(t') - \rho'_{-m,-m}(t') e^{-2i\mathcal{B}(t')}] dt'. \quad (5.2)$$

Substituting now (5.2) for $\rho'_{+n,-n}(t)$ into the formal solution for $\rho'_{+n,+n}(t)$, taking bath averages and making the noninteracting-blip approximation similar to that in Sec. IV, one obtains

$$\begin{aligned} \sigma_n(t) = & \sum_m G_{nm}(t) \sigma_m(0) \\ & - \int_0^t dt' \int_0^{t'} dt'' \sum_m (\Delta_m/\bar{\Delta}) G_{nm}(t-t') \sum_l (\Delta_l/\bar{\Delta}) G_{ml}(t'-t'') [\bar{h}(t'-t'') p_l(t'') + \bar{g}(t'-t'') \sigma_l(t'')], \end{aligned} \quad (5.3)$$

where $p_n(t)$ again follows from (4.9) and

$$\begin{aligned} \bar{g}(t) &= \bar{\Delta}^2 \cos(\epsilon t/\hbar) \cos \vartheta(t) e^{-\gamma(t)}, \\ \bar{h}(t) &= \bar{\Delta}^2 \sin(\epsilon t/\hbar) \sin \vartheta(t) e^{-\gamma(t)}. \end{aligned} \quad (5.4)$$

This result generalizes (4.10) to the case of a nonzero bias. Notice that if $\epsilon=0$ one has $\bar{h}(t)=0$ while $\bar{g}(t)$ becomes equal to the kernel $\bar{f}(t)$ of Sec. IV C. The kernels (5.4) are *exactly* identical to those for the single-site spin-boson system [10].

If the hopping rate is fast compared to the on-site dynamics one may again set $G_{nm}(t) = p_n^e$, and writing $\sigma_n(t) = p_n^e X(t)$ then also maps the biased case onto the corresponding *effective* single-site problem. For instance, making use of a theorem by Leggett *et al.* [10] concerning the ratio of Laplace transforms $\bar{h}(s)/\bar{g}(s)$, one has $\sigma_n(\infty) = -p_n^e \tanh(\beta\epsilon/2)$. If $\alpha > 1$ the polarization always relaxes to this value exponentially at a rate $\bar{\Gamma} = \bar{g}(s=0)$. For further details see Refs. [10] and [32].

VI. FINAL REMARKS

In this article an *ab initio* analysis has been presented of the quantum-mechanical dissipative double-well system at finite temperatures. The present treatment does *not* involve the usual two-level (ground-state-doublet) approximation. The theory provides a unified picture of the tunneling process and the vibrational dynamics. The latter give rise to an interdoublet stochastic hopping process (on the energy lattice). The former imply an intradoublet dissipative pseudospin dynamics (at each lattice site).

In Sec. II the model Hamiltonian following Zwanzig-Caldeira-Leggett has been introduced, and the (partially) reduced density-operator equation is derived. In Sec. III this equation is then written in terms of the energy (or, alternatively, the “localized-states”) representation. The *interdoublet* vibrational dynamics is evaluated making only (i) the local harmonic approximation, and (ii) the secular (or coarse-graining) approximation. The *intra-*

doublet dynamics is evaluated in Sec. IV by implementing appropriately adapted versions of the displaced-bath-oscillator basis and noninteracting-blip approximation.

The extension of the theory to the case of a nonzero

bias energy between left- and right-hand localized states is given in Sec. V. The ultimate result is given in (5.3), which upon differentiation with respect to time may also be written as

$$\dot{\sigma}_n(t) = \sum_m W_{nm} \sigma_m - \int_0^t dt' \sum_m (\Delta_n \Delta_m / \bar{\Delta}^2) G_{nm}(t-t') [\bar{h}(t-t') p_m(t') + \bar{g}(t-t') \sigma_m(t')] , \quad (6.1)$$

where $p_n(t) = \sum_m G_{nm}(t) p_m(0)$ is the solution of $\dot{p}_n = \sum_m W_{nm} p_m$, the W_{nm} being specified in (3.11). In the zero-hopping limit [$W_{nm} = 0$, i.e., $G_{nm}(t) = \delta_{nm}$] one retrieves the known single-site behavior. In an exhaustive account (available upon request [32]), it is also shown how the theory may be extended to the classical (thermal activation) regime.

In conclusion, this paper provides a rather complete solution of the dynamics of the dissipative double-well system described by the Hamiltonian (2.1).

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APPENDIX

Quantum diffusion coefficient

In this appendix we calculate the diffusion coefficient $D_{pp} = D_{pp}(t = \infty)$ as occurring in (3.11). *Inter alia* a compact novel formula will be presented. Related material can be found in Refs. [16,24,32–36]. The following heavily leans on Chap. 5 of Ref. [16].

Taking the environmental averages (2.12) in (2.9) for the local harmonic oscillator (i.e., $H_0 = \frac{1}{2}p^2 + \frac{1}{2}\omega_0^2 \xi^2$) yields [16,32,35]

$$\begin{aligned} \dot{\rho} = & -\frac{i}{\hbar} [H_0, \rho] - \frac{i}{\hbar} \lambda [\xi, [p, \rho]_+] + (2/\hbar^2) D_{px}(t) [p, [\xi, \rho]] \\ & - (1/\hbar^2) D_{pp}(t) [\xi, [\xi, \rho]] , \end{aligned} \quad (A1)$$

where

$$\begin{aligned} D_{px}(t) &= \frac{1}{4} \langle \xi(t) \mathcal{F}(t) + \mathcal{F}(t) \xi(t) \rangle , \\ D_{pp}(t) &= \frac{1}{2} \langle p(t) \mathcal{F}(t) + \mathcal{F}(t) p(t) \rangle , \end{aligned} \quad (A2)$$

and where we have again written ρ for $\langle \rho \rangle$. The significance of $D_{px}(t)$ and $D_{pp}(t)$ as diffusion coefficients is most clearly seen by writing (A1) in the Wigner representation [16,33,38]. For the secular hopping process only $D_{pp}(t = \infty)$ matters.

In view of the linearity of the oscillator problem one can solve the corresponding quantum Langevin equations

$$\begin{aligned} \dot{\xi} &= p , \\ \dot{p} &= -\omega_0^2 \xi - 2\lambda p + \mathcal{F}(t) , \end{aligned} \quad (A3)$$

explicitly for $\xi(t)$ and $p(t)$. One finds [16]

$$\begin{aligned} \xi(t) &= \sum_k c_k \left[\frac{\hbar}{2\omega_k} \right]^{1/2} [a_k \phi_k(t) + \text{c.c.}] , \\ \phi_k(t) &= \frac{1}{\omega_k^2 - \omega_0^2 + 2i\lambda\omega_k} [e^{-i\omega_k t} - \gamma_k e^{-\lambda t - i\bar{\omega} t} \\ &\quad - (1 - \gamma_k) e^{-\lambda t + i\bar{\omega} t}] , \end{aligned} \quad (A4)$$

$$\gamma_k = (\omega_k + \bar{\omega} + i\lambda) / 2\bar{\omega} ,$$

where $\bar{\omega} = (\omega_0^2 - \lambda^2)^{1/2}$. With $p = \dot{\xi}$ and $\mathcal{F}(t)$ given in (2.10) this yields

$$D_{pp}(t) = -\frac{\hbar}{\pi} \int_0^\infty d\omega J(\omega) \coth(\frac{1}{2}\beta\hbar\omega) \text{Re}[\dot{\phi}(\omega, t) e^{i\omega t}] , \quad (A5)$$

where $J(\omega) = 2\lambda\omega f(\omega/\omega_c)$. Using $f = \exp(-\omega/\omega_c)$ with $\omega_c \rightarrow \infty$, the least convergent part of the integral allows for an elementary integration of its zero-point term, while its thermal contribution has been tabulated (Ref. [39] form.3.911.2). One obtains

$$D_{pp}(t) = D_{pp}(\infty) + 2\frac{\lambda}{\beta} e^{-\lambda t} \text{Im} \left[\frac{\lambda + i\bar{\omega}}{\bar{\omega}} e^{-i\bar{\omega}t} \right] \left[\coth \left[\frac{\pi t}{\beta\hbar} \right] - \frac{1}{1 + (\omega_c t)^2} \frac{\beta\hbar}{\pi t} \right] - \frac{\lambda}{\pi} e^{-\lambda t} \text{Im} \left[\frac{(\lambda + i\bar{\omega})^2}{\bar{\omega}} \int_{-\infty}^{\infty} \frac{\hbar}{\omega - \bar{\omega} + i\lambda} e^{i(\omega - \bar{\omega})t} \coth(\frac{1}{2}\beta\hbar\omega) d\omega \right], \quad (\text{A6})$$

where the imaginary part has been defined for real $\bar{\omega}$. The remaining integral can be evaluated by contour integration for $t > 0$. In view of $t=0$ exponentially regularizing the summation over the pertinent Matsubara frequencies $\nu_n = n\nu$ ($\nu = 2\pi/\beta\hbar$) and using the power-series definition of the hypergeometric function [39], the result may be written as

$$D_{pp}(t) = D_{pp}(\infty) + 2\frac{\lambda}{\beta} e^{-\lambda t} \text{Im} \left[\frac{\lambda + i\bar{\omega}}{\bar{\omega}} e^{-i\bar{\omega}t} \right] \left[\coth \left[\frac{\pi t}{\beta\hbar} \right] - \frac{1}{1 + (\omega_c t)^2} \frac{\beta\hbar}{\pi t} + 1 - 2F(\alpha, 1; 1 + \alpha; x) \right], \quad (\text{A7})$$

where $\alpha = (\lambda + i\bar{\omega})/\nu$ and $x = \exp[-\nu(t + \tau_c)]$, with $\tau_c = \omega_c^{-1}$. Since (A5) implies $D_{pp}(0) = 0$, the as yet unspecified $D_{pp}(\infty)$ becomes

$$D_{pp}(\infty) = -2\frac{\lambda}{\beta} \text{Im} \left[\frac{1 - 2F(\alpha, 1; 1 + \alpha; e^{-\nu\tau_c})}{\bar{\omega}} \nu\alpha \right]. \quad (\text{A8})$$

In the limit $\nu\tau_c = 2\pi k_B T / \hbar\omega_c \rightarrow \infty$ one obviously recovers the classical result $D_{pp}(\infty) = 2\lambda k_B T$, because $F(\alpha, \ell; c; 0) = 1$. However, since also $F(0, \ell; c; x) = 1$, the classical regime is actually reached already if $\nu \gg \max(\lambda, \bar{\omega})$. Further, using the pertinent formula [39] for $F(\alpha, \ell; \alpha + b; x)$ for $x \rightarrow 1$ (i.e., $\tau_c \rightarrow 0$) one finds

$$D_{pp}(\infty) = -2\frac{\lambda}{\beta} \text{Im} \left[\frac{\lambda + i\bar{\omega}}{\bar{\omega}} \{ 1 + 2\alpha [\gamma_E + \psi_E(\alpha) + \ln(\nu\tau_c)] \} \right], \quad (\text{A9})$$

where $\psi_E(\alpha)$ is the psi function and $\gamma_E = 0.5772 \dots$ is Euler's constant. In the "weak" classical limit [40] $|\alpha| \ln(\nu\tau_c) \rightarrow 0$ one recovers $D_{pp}(\infty) = 2\lambda k_B T$ while in the quantum limit $\alpha \rightarrow \infty$ the result may be given as

$$D_{pp}(\infty) = \frac{2\hbar\lambda}{\pi} \left[\frac{\bar{\omega}^2 - \lambda^2}{2\bar{\omega}} \text{arccot} \left[-\frac{\bar{\omega}^2 - \lambda^2}{2\lambda\bar{\omega}} \right] + 2\lambda \ln \left[\frac{\omega_c}{\omega_0} \right] \right], \quad (\text{A10})$$

which agrees with Refs. [24,34–36]. A detailed analysis of the enormous accuracy with which $D_{pp}(t_p)$ may be replaced by its steady-state value (on the time scale of the coarse-grained spin dynamics) is given in Ref. [32].

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