Phonon bottleneck in the low-excitation limit

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The phonon-bottleneck problem in the relaxation of two-level systems (spins) via direct phonon processes is considered numerically in the weak-excitation limit where the Schrödinger equation for the spin-phonon system simplifies. The solution for the relaxing spin excitation $p(t)$, emitted phonons $n_{\mathbf{k}}(t)$, etc., is obtained in terms of the exact many-body eigenstates. In the absence of phonon damping $\Gamma_{\rm ph}$ and inhomogeneous broadening, $p(t)$ approaches the bottleneck plateau $p_\infty > 0$ with strongly damped oscillations, the frequency being related to the spin-phonon splitting Δ at the avoided crossing. For any $\Gamma_{\rm ph} > 0$, one has $p(t) \to 0$, but in the case of strong bottleneck, the spin relaxation rate is much smaller than $\Gamma_{\rm ph}$ and $p(t)$ is nonexponential. Inhomogeneous broadening exceeding Δ partially alleviates the bottleneck and removes oscillations of $p(t)$. The linewidth of emitted phonons as well as Δ increase with the strength of the bottleneck, i.e., with the concentration of spins.

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I. INTRODUCTION

Spin-lattice relaxation is an old and much studied problem that currently received a resurge in attention because of its vital importance in quantum information processing (see, e.g., Ref. 1, and references therein). Theoretical description of the spin-lattice relaxation as a single-spin process is, in many cases, insufficient because of the collective effects of incoherent and coherent nature, such as the phonon bottleneck[2] and superradiance,[3] respectively.

The problem of phonon bottleneck (PB) in relaxation of two-level systems (henceforth spins) via direct phonon emission and/or absorption processes, first recognized by Van Vleck[2] in 1941, remains unsolved until now. In short, if the emitted phonons have nowhere to go, they are absorbed by spins again and, thus, the spins cannot relax efficiently. However transparent this picture might appear, it is not easy to propose a theoretical description of the effect based on first principles.

Published theories of the PB[4–8] use *ad hoc* rate equations for populations of spins and resonant phonons, considering the latter as a single dynamical variable. This is certainly an oversimplification, because the emitted phonons, having frequencies $\omega_{\mathbf{k}}$, form a group with a bell-like line shape with some width, centered around the spin transition frequency ω_0. For a single spin embedded into an infinite elastic matrix (as well as for a decaying atomic state in free space), this line shape is Lorentzian with the width $\Gamma/2$, where Γ is the single-spin decay rate following the Fermi golden rule.[9,10] However, in the case of many spins with a concentration sufficient to create a bottleneck, the line shape and linewidth of emitted phonons are unknown and should follow from the solution of the problem.

Van Vleck came to the idea of the phonon bottleneck comparing the rate of energy transfer from spins to phonons (obtained using experimental data) with the phonon relaxation rate $\Gamma_{\rm ph}$ due to different mechanisms, and he found the latter to be typically too small to keep the phonon subsystem at equilibrium. However, the primary role in the PB problem belongs to another parameter that is not related to the phonon relaxation rate. This parameter is of a statistical origin and is defined as the ratio of the number of spins to the number of phonon modes within the single-spin linewidth Γ.[11] If this so-called bottleneck parameter B is vanishingly small, the spin excitation goes over into the phonon subsystem and never returns. In this case, spins completely relax even without any phonon damping. However, for nonzero B and $\Gamma_{\rm ph} = 0$, the spin relaxation ends in the so-called bottleneck plateau that corresponds to a quasiequilibrium between spins and resonant phonons, but not to the complete equilibrium. Further relaxation to the complete equilibrium can be achieved only if $\Gamma_{\rm ph}$ is taken into account. It should be stressed that the effective relaxation rate of the spins in this case is not $\Gamma_{\rm ph}$. It is much smaller, and can be estimated as $\Gamma_{\rm ph}$ multiplied by the small fraction of phonon modes in the total number of modes (phonons+spins) involved in the process.

Although in many practical situations the number of resonant phonon modes is determined by the inhomogeneous broadening of spin levels, the pure spin-phonon model without inhomogeneous broadening has a fundamental importance. It was shown[11] that this model cannot be described *kinetically* (i.e., in terms of spin and phonon *populations* only) because of long-memory effects. In Ref. 11, memory effects have been taken into account within a minimal approximation, adding a new variable that can be interpreted as spin-phonon correlator. Analytical and numerical solutions of the resulting *reversible dynamical* equations show that the spin excitation approaches the bottleneck plateau with damped oscillations. Inclusion of an *ad hoc* phonon damping $\Gamma_{\rm ph}$ into the bottleneck equations allows one to describe the second stage of the relaxation toward the complete equilibrium.

Still, the solution of the PB problem in Ref. 11 is not completely satisfactory since it cannot produce a well-behaved line shape of emitted phonons. This indicates that additional nondiagonal correlators should be taken into account that will make the description more complicated. An-

other important factor that should be taken into account is the inhomogeneous broadening of the spin levels.

This paper presents the exact numerical solution of the phonon-bottleneck problem based on the Schrödinger equation for the spin-phonon system, with and without the *ad hoc* phonon damping and inhomogeneous spin broadening. The full Schrödinger equation for a many-body system is, of course, intractable by direct methods because of too many variables. However, the *low-excited* states of the system can be described by a *single excitation* that is hopping between spins and phonon modes. In this case, the Hilbert space of the problem is severely truncated, and one has to work with matrices the size of which is just the total number of spins and phonon modes under consideration. This is the case considered here, and the solution of the PB problem is obtained by matrix algebra using Wolfram MATHEMATICA. The results of the calculations show that for the pure model, the spin excitation approaches the bottleneck plateau with oscillations, however, less revealed than in Ref. 11. The linewidth of emitted phonons broadens with the bottleneck parameter B.

The structure of the rest of the paper is the following. Section II sets up the Hamiltonian of the spin-phonon system and the Schrödinger equation (SE) in the case of a single excitation. The spin excitation and the initial conditions for the problem are defined here. Section III presents the known results for the relaxation of a *single spin* and for the energy distribution of emitted phonons, used later for reference. Section IV introduces the bottleneck parameter B for systems of many spins from statistical arguments, both with and without inhomogeneous spin broadening. Section V is the central section of the paper introducing the matrix formalism for the single-excitation spin-phonon problem. Here, the expressions for the spin excitation $p(t)$, its asymptotic value p_∞ (the bottleneck plateau), and the asymptotic populations of the emitted phonons are obtained in terms of eigenvectors and eigenvalues of the dynamical matrix of the system. General analysis of the eigenstates of the dynamical matrix is done in Sec. VI. It is shown here that the number of the phonon modes "on speaking terms" with spins for the pure problem increases with B, thus changing the statistical balance between spins and phonon modes. In this section, the formulas describing the spectrum of the *split spin-phonon modes* and the hybridization of different phonon modes with each other (i.e., the scattering of phonons on spins) are obtained in terms of the eigenstates of the dynamical matrix. Section VII presents the results of numerical calculations for the pure model, including the split spin-phonon modes with the gap, time evolution of the spin excitation, bottleneck plateau, the postplateau relaxation due to the phonon damping, and the energy distribution of the emitted phonons in the pure model. In Sec. VIII, the effects of the inhomogeneous spin broadening are considered. The latter is shown to wash out oscillations of the spin excitation $p(t)$. Section IX contains the implementation of the general results to the spin relaxation between adjacent spin levels in molecular magnets. In Sec. X, further problems of collective spin-phonon relaxation are discussed.

II. HAMILTONIAN AND SCHRÖDINGER EQUATION

Consider a spin-phonon Hamiltonian for N_S two-level systems (spins) placed at positions $\mathbf{r}_i$ within an elastic body of N cells

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{1}$$

where

$$\hat{H}_0 = -\frac{1}{2}\sum_i \hbar\omega_{0i}\sigma_{iz} + \sum_{\mathbf{k}} \hbar\omega_{\mathbf{k}} a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \tag{2}$$

describes spins and harmonic phonons, $\boldsymbol{\sigma}$ being the Pauli matrix. The spin transition frequencies ω_i can differ from site to site. One can represent them in the form

$$\omega_{0i} = \overline{\omega_0} + \delta\omega_{0i}, \tag{3}$$

where $\delta\omega_{0i} \ll \overline{\omega_0}$ is the inhomogeneous broadening. Everywhere except Sec. VIII, we will use ω_0 as the spin transition frequency instead of $\overline{\omega_0}$. Neglecting the processes that do not conserve the energy (that can be done in cases of practical significance, where $\hat{V}$ can be treated as a perturbation), one can write $\hat{V}$ in the rotating-wave approximation (RWA) as

$$\hat{V} = -\frac{\hbar}{\sqrt{N}}\sum_i \sum_{\mathbf{k}} (A_{i\mathbf{k}}^* X_i^{01} a_{\mathbf{k}}^\dagger + A_{i\mathbf{k}} X_i^{10} a_{\mathbf{k}}), \tag{4}$$

where $A_{i\mathbf{k}} \equiv V_{\mathbf{k}} e^{-i\mathbf{k}\cdot r_i}$. In the numerical work below, $V_{\mathbf{k}}$ will be replaced by a constant, $V_{\mathbf{k}} \Rightarrow V$. The operator $X^{10} \equiv \sigma_-$ brings the spin from the ground state $|\uparrow\rangle \equiv |0\rangle \equiv \binom{1}{0}$ to the excited state $|\downarrow\rangle \equiv |1\rangle \equiv \binom{0}{1}$, while $X^{01} \equiv \sigma_+$ does the opposite. Note that the state with no phonons and all spins in the ground state is the true ground state of the Hamiltonian above.

Below, we will consider the low-excited states of the spin-phonon system that can be described by a superposition of the vacuum state of the system $|0\rangle$ (no phonons and all spins in the ground state) and the states with one excitation that is hopping between the spins and phonon modes. The wave function of these states has the form

$$\Psi = \left(c_0 + \sum_i c_i X_i^{10} + \sum_{\mathbf{k}} c_{\mathbf{k}} a_{\mathbf{k}}^\dagger\right)|0\rangle, \tag{5}$$

where the coefficients satisfy the system of equations

$$\frac{dc_0}{dt} = i\omega_0 c_0 \tag{6}$$

and

$$\dot{c}_i = -i\,\delta\omega_{0i} c_i + \frac{i}{\sqrt{N}}\sum_{\mathbf{k}} A_{i\mathbf{k}} c_{\mathbf{k}},$$

$$\dot{c}_{\mathbf{k}} = -i\left(\omega_{\mathbf{k}} - \frac{i}{2}\Gamma_{\mathrm{ph}} - \omega_0\right)c_{\mathbf{k}} + \frac{i}{\sqrt{N}}\sum_i A_{i\mathbf{k}}^* c_i \tag{7}$$

up to an irrelevant global phase factor. In the second equation, an *ad hoc* phonon damping Γ_{ph} is included. Using a damped Schrödinger equation for phonons can be justified only at sufficiently low temperatures, so that only outgoing

terms in phonon relaxation play a role. Even in this case, this equation cannot be taken for granted because only *inelastic* phonon processes should play a significant role in the PB, while elastic processes do not lead to exchange of excitation between resonant phonons and the rest of the phonon bath.

One can see that the ground-state coefficient c_0 is decoupled from the other coefficients since the RWA Hamiltonian conserves the excitation number

$$p(t) + \sum_{\mathbf{k}} n_{\mathbf{k}}(t) = \text{const}, \tag{8}$$

where

$$p = \sum_i |c_i|^2, \quad n_{\mathbf{k}} = |c_{\mathbf{k}}|^2 \tag{9}$$

are the excitation number of the spin subsystem and populations of the phonon modes. One can also define transverse spin polarization components by

$$\langle \sigma_+ \rangle = \langle X^{01} \rangle = c_0^* \sum_i c_i$$

$$\langle \sigma_- \rangle = \langle \sigma_+ \rangle^*, \quad \langle \sigma_x \rangle = \mathrm{Re}\langle \sigma_+ \rangle, \tag{10}$$

etc. The main part of the time dependence of $\langle \sigma_+ \rangle$ is $e^{-i\omega_0 t}$. The absolute value of the transverse spin component

$$\langle \sigma_\perp \rangle \equiv \sqrt{\langle \sigma_x \rangle^2 + \langle \sigma_y \rangle^2} = |\langle \sigma_+ \rangle| \tag{11}$$

does not have this oscillating factor. In many practical situations, $\langle \sigma_\perp \rangle$ decays with time due to inhomogeneous broadening. In the absence of the latter, the only source of the decoherence is interaction with phonons.

Our task is to find the time evolution $p(t)$ and $\langle \sigma_\perp \rangle_t$ starting from a particular initial state. In this work, we restrict ourselves to the initial states with no phonons, $c_{\mathbf{k}}(0)=0$. The simplest initial condition in this case is one spin at site i_0 excited and all other spins in their ground states:

$$c_{i_0}(0) = 1, \quad c_{i \neq i_0}(0) = 0. \tag{12}$$

Another kind of the initial spin state is the state with the excitation equally distributed over all spins:

$$c_i(0) = e^{i\phi_i}/\sqrt{N_S}. \tag{13}$$

The initial spin state with random phases,

$$\langle e^{i(\phi_i - \phi_j)} \rangle = \delta_{ij}, \tag{14}$$

is called incoherent. If ϕ_i are constant or they periodically change in space with some wave vector $\mathbf{q}_0$, the initial state is coherent. One can consider other kinds of spin initial conditions, say, excitation distributed over spins in some compact region of space.

III. NONBOTTLENECKED SPIN-LATTICE RELAXATION

The results of this section can be found in the literature,[9,10] still a concise description of the nonbottlenecked spin-phonon dynamics is presented for the sake of consistency and future reference.

A. Relaxation of a single spin

Suppose there is a single spin, $c_i=c$, in the initially excited state. With a proper choice of the origin of the coordinate system, one has $A_{i\mathbf{k}}=V_{\mathbf{k}}$. Using the Schrödinger equation (7) with $\Gamma_{\mathrm{ph}} \to 0$, one can integrate the equations for the phonon modes $c_{\mathbf{k}}$:

$$c_{\mathbf{k}}(t) = \frac{iV_{\mathbf{k}}^*}{\sqrt{N}} \int_{t_0}^{t} dt' e^{-i(\omega_{\mathbf{k}} - \omega_0)(t-t')} c(t')$$

$$= \frac{iV_{\mathbf{k}}^*}{\sqrt{N}} \int_0^{t-t_0} d\tau e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau} c(t-\tau) \tag{15}$$

and insert the result into the equation for the spin c:

$$\dot{c} = -\frac{1}{N} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \int_0^{t-t_0} d\tau e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau} c(t-\tau). \tag{16}$$

In this integrodifferential equation, $c(t-\tau)$ is a slow function of time, whereas the memory function $f(\tau) = (1/N)\Sigma_{\mathbf{k}} |V_{\mathbf{k}}|^2 e^{-i(\omega_{\mathbf{k}} - \omega_0)\tau}$ is sharply peaked at $\tau=0$. Thus, one can replace $c(t-\tau) \Rightarrow c(t)$, after which integration over τ and keeping only real contribution responsible for the relaxation yields the equation

$$\dot{c} = -\frac{\Gamma}{2} c, \tag{17}$$

where

$$\Gamma = \frac{2\pi}{N} \sum_{\mathbf{k}} |V_{\mathbf{k}}|^2 \delta(\omega_{\mathbf{k}} - \omega_0) \tag{18}$$

is the single-spin decay rate. For $V_{\mathbf{k}}=V$ independent of the direction of $\mathbf{k}$, Γ can be written as

$$\Gamma = 2\pi |V|^2 \rho_{\mathrm{ph}}(\omega_0), \tag{19}$$

where

$$\rho_{\mathrm{ph}}(\omega) = \frac{1}{N} \sum_{\mathbf{k}} \delta(\omega_{\mathbf{k}} - \omega) \tag{20}$$

is the phonon density of states normalized by 1. The accuracy of the above short-memory approximation is justified by $\Gamma \ll \omega_0$. The δ function in Eq. (18) implies that the spin is relaxing to a large number of phonon modes so that summation is replaced by integration,

$$\frac{1}{N} \sum_{\mathbf{k}} \ldots \Rightarrow \int \frac{d^d k}{(2\pi)^d} \ldots, \tag{21}$$

where d is spatial dimension. In small bodies with essentially discrete phonon modes, Eq. (21) is invalid. The solution of Eq. (17) with $t_0=0$ is $c(t)=e^{-(\Gamma/2)t}$, which leads to a well-known decay rule for the spin excitation

$$p(t) = e^{-\Gamma t}. \tag{22}$$

The rate of transverse spin relaxation according to Eqs. (10) and (17) is $\Gamma/2$.

A similar elimination of phonons can be performed in the case of many spins in the absence of the PB.[12] The resulting

equations describe collective spin-phonon relaxation, including superradiance.[3]

B. Distribution of emitted phonons

After the time dependence $c(t)$ has been found, one can return to Eq. (15) and calculate $c_{\mathbf{k}}(t)$. With $t_0=0$, the result is

$$c_{\mathbf{k}}(t)=\frac{iV_{\mathbf{k}}^*}{\sqrt{N}}\frac{e^{-i(\omega_{\mathbf{k}}-\omega_0)t}-e^{-\Gamma t/2}}{-i(\omega_{\mathbf{k}}-\omega_0)+\Gamma/2}. \tag{23}$$

This leads to the distribution of emitted phonons

$$n_{\mathbf{k}}(t)=|c_{\mathbf{k}}(t)|^2=\frac{|V_{\mathbf{k}}|^2}{N}\frac{1-2e^{-\Gamma t/2}\cos[(\omega_{\mathbf{k}}-\omega_0)t]+e^{-\Gamma t}}{(\omega_{\mathbf{k}}-\omega_0)^2+\Gamma^2/4} \tag{24}$$

that asymptotically becomes the Lorentzian function

$$n_{\mathbf{k}}=\frac{1}{N}\frac{|V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}}-\omega_0)^2+\Gamma^2/4}. \tag{25}$$

With the help of Eqs. (22) and (24), one can check that the total excitation is conserved, in accordance with Eq. (8). For $V_{\mathbf{k}}=V$, Eq. (25) can be rewritten as

$$n_{\mathbf{k}}=\frac{1}{\pi N\rho_{\mathrm{ph}}(\omega_0)}\frac{\Gamma/2}{(\omega_{\mathbf{k}}-\omega_0)^2+\Gamma^2/4}. \tag{26}$$

IV. PHONON BOTTLENECK

Let us now turn to systems with a macroscopic number of spins N_S. At least in the case of diluted spins, the relaxation is controlled by the bottleneck parameter B that can be defined as the ratio of the number of spins N_S to the number of phonon modes N_Γ within the natural spin linewidth Γ of Eq. (18),

$$N_\Gamma=\pi N\rho_{\mathrm{ph}}(\omega_0)\Gamma, \tag{27}$$

where $\rho_{\mathrm{ph}}(\omega)$ is given by Eq. (20). That is,[11]

$$B\equiv\frac{N_S}{N_\Gamma}=\frac{N_S}{\pi N\rho_{\mathrm{ph}}(\omega_0)\Gamma}=\frac{n_S}{\pi\rho_{\mathrm{ph}}(\omega_0)\Gamma}, \tag{28}$$

$n_S=N_S/N$ being the number of spins per unit cell. The definitions above pertain to a single phonon branch, and extension to several phonon branches is obvious. For $B\lesssim 1$ (see below), N_Γ is the estimation of the number of phonon modes that can exchange excitation with spins.

In the case of a single spin, $N_S=1$, in a macroscopic ($N\to\infty$) matrix, the parameter B is vanishingly small. The excitation, initially localized at the spin, spreads with time over a large number N_Γ of resonant phonon modes, so that the spin relaxes completely according to Eq. (22). In simulations, the macroscopic limit is achieved if the average distance between the neighboring phonon modes becomes smaller than the natural linewidth Γ

$$\frac{1}{N\rho_{\mathrm{ph}}(\omega_0)}\ll\Gamma. \tag{29}$$

If the sample is so small that the spin can exchange excitation with only a few phonon modes, $N_\Gamma\sim 1$, it does not relax completely. In this case, one has $B\sim 1$, the so-called phonon-bottleneck situation. The simplest realization of the bottleneck is a system of two resonant states in which the excitation oscillates between the two states in time. If N_S is macroscopic but still $N_S\ll N_\Gamma$ and, thus, $B\ll 1$, the initial spin excitation is transferred irreversibly into the phonon subsystem, as is clear from statistical arguments. There is no bottleneck for $B\ll 1$, and the spin relaxation is still described by Eq. (22).

In the case of a finite concentration of spins n_S, the parameter B can easily become large. In this case, only a small fraction of the excitation migrates into the phonon subsystem and the spins practically cannot relax as the emitted phonons are being absorbed by spins again. For $B\gg 1$, as we will immediately see, the number of the phonon modes on speaking terms with spins is not N_Γ but much greater. The latter can be obtained if one considers the spin-phonon hybridization. Inserting the spin Fourier components $b_{\mathbf{k}}\equiv\Sigma_i c_i e^{i\mathbf{k}\cdot\mathbf{r}_i}$ into the Schrödinger equation (7) and neglecting the coupling of modes with different values of $\mathbf{k}$, i.e., using $\Sigma_i\nu_i e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i}\Rightarrow N_S\delta(\mathbf{k}-\mathbf{q})$ ($\nu_i=1$ if site i is occupied by a spin and zero otherwise), one can reduce Eq. (7) to a 2×2 matrix problem that can be easily diagonalized. The eigenstates of this problem are hybridized spin-phonon modes with frequencies[13,14]

$$\Omega_{\mathbf{k}}^{(\pm)}=\frac{1}{2}\{\omega_{\mathbf{k}}-\omega_0\pm\sqrt{(\omega_{\mathbf{k}}-\omega_0)^2+\Delta_{\mathbf{k}}^2}\}, \tag{30}$$

where

$$\Delta_{\mathbf{k}}=2\sqrt{n_S}|V_{\mathbf{k}}| \tag{31}$$

is the spin-phonon splitting. These modes have the form of a straight line with a slope corresponding to phonons and a horizontal line corresponding to spins. The lines have an avoided level crossing at $\omega_{\mathbf{k}}=\omega_0$, split by $\Delta_{\mathbf{k}}$ that depends on the spin concentration. For $V_{\mathbf{k}}=V$ independent of the direction of $\mathbf{k}$, one can eliminate $\rho_{\mathrm{ph}}(\omega_0)$ from Eq. (28) with the help of Eqs. (20) and (18), and obtain the relation

$$B=\frac{2n_S|V|^2}{\Gamma^2}=\frac{\Delta^2}{2\Gamma^2}. \tag{32}$$

For $\Delta\gtrsim\Gamma$, the number of phonon modes strongly coupled to spins can be estimated as

$$N_\Delta=\pi N\rho_{\mathrm{ph}}(\omega_0)\frac{\Delta}{2}. \tag{33}$$

If n_S is so small that Δ falls below the natural spin linewidth Γ, one cannot speak of the hybridized spin-phonon modes. From Eq. (32), one obtains

$$N_\Delta=N_\Gamma\sqrt{B/2}. \tag{34}$$

The number of resonant phonons N_{res} that exchange excitation with the spins can be estimated in the whole range of B as

$$N_{\mathrm{res}}=\begin{cases}N_\Gamma, & B\lesssim 1\\ N_\Delta, & B\gtrsim 1.\end{cases} \tag{35}$$

For any $B>0$, the spin excitation $p(t)$ does not relax to zero but reaches a plateau at some p_∞ that, from the statistical equidistribution argument, can be estimated as

$$p_\infty = \frac{N_S}{N_S + N_{\rm res}}, \tag{36}$$

with $N_{\rm res}$ defined above. We will see that this formula works well both for $B \lesssim 1$ and $B \gtrsim 1$, in the absence of the inhomogeneous broadening that will be considered in Sec. VIII. The asymptotes of the above expression are

$$p_\infty \cong \begin{cases} B, & B \ll 1 \\ 1 - 1/\sqrt{2B}, & B \gg 1, \end{cases} \tag{37}$$

in accordance with the numerical results of Sec. VII.

To describe the complete spin relaxation after the bottleneck plateau, one has to include the phonon relaxation processes, the easiest way being ascribing an empirical relaxation rate $\Gamma_{\rm ph}$ to the phonons, as was done in Eq. (7). The condition for suppression of the PB by the phonon damping and recovering the single-spin relaxation, Eq. (22), in the case $B \gg 1$ has the form[11]

$$\sigma \equiv \frac{\Delta}{\Gamma_{\rm ph}} \ll 1, \tag{38}$$

where Δ is the average spin-phonon splitting $\Delta_{\mathbf{k}}$ [see Eqs. (30) and (31)]. The ratio σ is another bottleneck parameter accounting for the phonon damping. With the help of Eq. (32), it can be rewritten in the form

$$\sigma \sim \frac{\sqrt{B}\Gamma}{\Gamma_{\rm ph}} = \frac{1}{\Gamma_{\rm ph}} \sqrt{\frac{n_S \Gamma}{\pi \rho_{\rm ph}(\omega_0)}} \ll 1. \tag{39}$$

Bottleneck parameters similar to but not coinciding with σ were used in literature[8] as part of *ad hoc* rate equations. It should be stressed that $\Gamma_{\rm ph}$ describes inelastic phonon processes that lead to exchange of excitation between the resonant phonons and the rest of the phonon bath. The phonon relaxation rate $\Gamma_{\rm ph}$ increases with frequency ω_0.

V. DYNAMIC MATRIX AND THE TIME EVOLUTION OF THE SYSTEM

For the numerical solution of Eq. (7), it is convenient to introduce the state vector $\mathbf{C}=(\{c_i\},\{c_{\mathbf{k}}\})$ and rewrite Eq. (7) in the form

$$\frac{d\mathbf{C}}{dt} = -i\mathbf{\Phi}\cdot\mathbf{C}, \tag{40}$$

where $\mathbf{\Phi}$ is the dynamical matrix of the spin-phonon system. In the absence of phonon damping, $\mathbf{\Phi}$ is Hermitian. Since the number of discrete phonon modes is N, $\mathbf{\Phi}$ is an $(N_S+N)\times(N_S+N)$ matrix. There are three methods of numerical solution of this equation that can be implemented in Wolfram MATHEMATICA.

The first method is the direct numerical solution using one of the ordinary-differential equation (ODE) solvers. This method is fast, can be made much faster if MATHEMATICA is replaced by one of programming languages, it does not require high accuracy, but it does not allow one to analytically average over the random phases in Eq. (13). This averaging can only be done if one runs the calculation many times with different realizations of initial conditions.

The second method is based on numerical calculation of the matrix exponentials in the solution of Eq. (40), $\mathbf{C}(t) = e^{-i\mathbf{\Phi}t}\mathbf{C}(0)$. This method is slower than the direct ODE solution, it also does not require high accuracy, and, here, one can average over the initial conditions analytically.

The third method uses the expansion of the solution $\mathbf{C}(t)$ over eigenvectors of $\mathbf{\Phi}$. This method allows analytical averaging over initial conditions; it is faster than the method using matrix exponentials if formulated in a fully vectorized form. However, this method requires high precision and, for large matrices, it runs on 64-bit machines only. Note that arbitrary-precision computations on 32-bit machines with MATHEMATICA are possible, but they are very slow. An important advantage of this method is that it allows one to obtain formulas for the asymptotic $t\to\infty$ state of the system in terms of matrices.

Below, the method based on the eigenvectors of $\mathbf{\Phi}$ will be used. In the general case when the *ad hoc* phonon damping $\Gamma_{\rm ph}$ is added, $\mathbf{\Phi}$ is non-Hermitian, and one has to distinguish between right and left eigenvectors. The dynamical matrix $\mathbf{\Phi}$ has N_S+N right eigenvectors $\mathbf{R}_\mu$ that satisfy

$$\mathbf{\Phi}\cdot\mathbf{R}_\mu = (\Omega_\mu - i\Gamma_\mu/2)\mathbf{R}_\mu. \tag{41}$$

In the eigenvalues, the imaginary parts $\Gamma_\mu/2$ originate from $\Gamma_{\rm ph}/2$ in Eq. (7). The size of the matrix $\mathbf{\Phi}$ can be reduced if the phonon modes far from the resonance are dropped. The solution of Eq. (40) can be expanded over the complete orthonormal set of $\mathbf{R}_\mu$ as follows:

$$\mathbf{C}(t) = \sum_\mu \mathbf{R}_\mu e^{-(i\Omega_\mu + \Gamma_\mu/2)t}\mathbf{L}_\mu\cdot\mathbf{C}(0), \tag{42}$$

where $\mathbf{L}_\mu$ are left eigenvectors of $\mathbf{\Phi}$ that satisfy $\mathbf{L}_\mu\cdot\mathbf{R}_\nu = \delta_{\mu\nu}$. Note that, in general, $\mathbf{R}_\mu$ and $\mathbf{L}_\mu$ are not complex conjugate. The vectorized form of Eq. (42) is

$$\mathbf{C}(t) = \mathbf{E}\cdot\mathbf{W}(t)\cdot\mathbf{E}^{-1}\cdot\mathbf{C}(0), \tag{43}$$

where $\mathbf{E}$ is the right-eigenvector matrix composed of all eigenvectors $\mathbf{R}_\mu$ standing vertically, $\mathbf{E}^{-1}$ is the left-eigenvector matrix, composed of all left eigenvectors lying horizontally, and $\mathbf{W}(t)$ is the diagonal matrix with the elements $e^{-(i\Omega_\mu+\Gamma_\mu)t}$. In fact, $\mathbf{E}\cdot\mathbf{W}(t)\cdot\mathbf{E}^{-1} = e^{-i\mathbf{\Phi}t}$.

A. Longitudinal relaxation of spins

Now the spin excitation $p(t)$ can be written with the help of Eqs. (9) and (43) in the vectorized form

$$p(t) = (\mathbf{E}\cdot\mathbf{W}(t)\cdot\mathbf{E}^{-1}\cdot\mathbf{C}(0))_S\cdot(\text{H.c.})_S, \tag{44}$$

where the subscript S means projection onto the spin subspace. Equation (44) can be used for a fast computation. For the incoherent initial condition, Eqs. (13) and (14), one obtains

$$p(t) = \frac{1}{N_S}\mathrm{Tr}_S[(\mathbf{E}\cdot\mathbf{W}(t)\cdot\mathbf{E}^{-1})_S\cdot(\mathrm{H.c.})_S], \tag{45}$$

where the trace is taken over spin indices only. A more explicit form of Eq. (44) is

$$p(t) = \sum_{\mu\nu} e^{-(\Gamma_\mu+\Gamma_\nu)t/2}\cos[(\Omega_\mu-\Omega_\nu)t]\sum_{n=1}^{N_S} R^*_{\mu n}R_{\nu n} \times \sum_{n'=1}^{N_S} L_{\nu n'}C_{n'}(0)\sum_{n''=1}^{N_S} L^*_{\mu n''}C^*_{n''}(0). \tag{46}$$

In the absence of phonon damping, $\Gamma_\mu=0$, there is a nonzero asymptotic value of p that can be obtained from the equation above by dropping all oscillating terms, i.e., setting $\mu=\nu$. This corresponds to the diagonal density matrix of the spin-phonon system. Taking into account $L^*_{\mu n}=R_{\mu n}$ in the Hermitian case, one obtains

$$p_\infty = \sum_\mu\sum_{n=1}^{N_S}|R_{\mu n}|^2\left|\sum_{n'=1}^{N_S} R^*_{\mu n'}C_{n'}(0)\right|^2. \tag{47}$$

For the incoherent initial condition, this simplifies to

$$p_\infty = \frac{1}{N_S}\sum_\mu\left(\sum_{n=1}^{N_S}|R_{\mu n}|^2\right)^2. \tag{48}$$

Note that in the macroscopic limit $N\to\infty$ for a single spin, Eq. (46) should assume the simple exponential form of Eq. (22) and $p_\infty=0$. The same should be the case for any finite N_S.

If the phonon damping Γ_{ph} is finite but small, the process of spin relaxation is two stage. First, the spin subsystem equilibrates with the subsystem of resonant phonons and $p(t)$ mainly changes due to the time dependence of the terms with $\mu\neq\nu$ in Eq. (46), whereas the role of Γ_μ is insignificant. At the end of this stage, the terms with $\mu\neq\nu$ die out, and the further slow relaxation is governed by Γ_μ. In particular, for the incoherent initial condition, Eq. (46) at the second stage of the relaxation becomes

$$p(t) = \frac{1}{N_S}\sum_\mu e^{-\Gamma_\mu t}\sum_{n=1}^{N_S}|R_{\mu n}|^2\sum_{n'=1}^{N_S}|L_{\mu n'}|^2. \tag{49}$$

Since for macroscopic systems the number of different values of Γ_μ in this expression is very large, the dependence $p(t)$ is a combination of many different exponentials, i.e., $p(t)$ is nonexponential.

In the limit we study in the paper, $k_0r_0\gg1$ (k_0 is the wave vector of a resonant phonon and r_0 is the typical distance between the neighboring spins), the solution $p(t)$ is actually the same for coherent and incoherent initial conditions. The only difference is that for the incoherent initial condition, averaging over the initial phases of spins leads to reproducible results for different realizations of the nondiagonal elements of $\mathbf{\Phi}$. For coherent initial conditions, one obtains somewhat different results for different realizations of the spin-phonon matrix elements, related to location of the individual spins in space. These differences persist with increasing number of spins and phonon modes, so that there is no self-averaging. The computation of $p(t)$ in the coherent case is faster, but averaging over spin configurations is needed.

B. Transverse relaxation of spins

Let us now consider the time evolution of the transverse spin polarization given by Eq. (11) starting from the fully coherent initial condition

$$c_i = \frac{\sin\theta}{\sqrt{N_S}}, \quad c_0 = \cos\theta \tag{50}$$

that satisfies the normalization condition $|c_0|^2+\Sigma_i|c_i|^2=1$ for the wave function of Eq. (5) in the case of initial phonon vacuum. In Eq. (50), θ is the angle between the spin vector and the z axis. In the initial state, one has

$$\langle\sigma_\perp\rangle_0 = \sqrt{N_S}\sin\theta\cos\theta \tag{51}$$

that can be used to define the normalized transverse spin polarization

$$f_\perp(t) = \langle\sigma_\perp\rangle_t/\langle\sigma_\perp\rangle_0 \tag{52}$$

that satisfies $f_\perp(0)=1$. With the help of Eq. (43), one obtains the vectorized expression

$$f_\perp(t) = \left|\frac{1}{N_S}\sum_{nn'=1}^{N_S}(\mathbf{E}\cdot\mathbf{W}(t)\cdot\mathbf{E}^{-1})_{nn'}\right|. \tag{53}$$

Note that this formula is explicitly independent of the angle θ. An alternative expression for $f_\perp(t)$ following Eq. (42) has the form

$$f_\perp(t) = \left|\sum_\mu T_\mu e^{-(i\Omega_\mu+\Gamma_\mu/2)t}\right|, \tag{54}$$

where

$$T_\mu \equiv \frac{1}{N_S}\sum_{n=1}^{N_S}R_{\mu n}\sum_{n'=1}^{N_S}L_{\mu n'}. \tag{55}$$

In the case of undamped phonons, one has $L^*_{\mu n}=R_{\mu n}$ and $T_\mu=(1/N_S)|\Sigma_{n=1}^{N_S}R_{\mu n}|^2$ is real. Then, dropping oscillating terms in Eq. (54) at large times, one obtains the asymptotic value $f_\perp(\infty)=\sqrt{\Sigma_\mu|T_\mu|^2}$ [cf. transition from Eq. (46) to Eq. (47)]. It can be easily shown that in the presence of inhomogeneous broadening and in the absence of the coupling to phonons, $f_\perp(\infty)\to0$ in the thermodynamic limit. The same should hold in the presence of both inhomogeneous broadening and spin-phonon interaction since the former should be sufficient to cause complete decoherence. Analysis of the principally important case without the inhomogeneous broadening should be postponed until numerical results. For a single spin, coupling to phonons causes decoherence with the rate $\Gamma/2$, as was stressed at the end of Sec. III A. In the case of the phonon bottleneck, this decoherence should be slowed down since a few phonon modes couple to many spins, still the expected result is $f_\perp(\infty)=0$.

C. Energy distribution of emitted phonons

The method formulated above can be used to find the state of the phonon system resulting from spin-phonon relaxation. Obviously, it can be done for undamped phonons only. In the case of many spins, there are no analytical results for the occupation numbers of emitted phonons $n_{\mathbf{k}}$ in the literature. However, one can express $n_{\mathbf{k}}$ through the eigenstates of the dynamical matrix $\mathbf{\Phi}$ defined by Eqs. (40) and (41). For the wave function given by Eq. (5), one has $n_{\mathbf{k}}=|c_{\mathbf{k}}|^2$. Labeling the phonon modes by the discrete index l, one can express $n_{\mathbf{k}}\equiv n_l$ through the state vector $\mathbf{C}$ given by Eq. (42). For the incoherent initial spin state with the help of Eq. (14), one obtains, asymptotically,

$$n_l(\infty)=\frac{1}{N_S}\sum_{\mu}\sum_{n=1}^{N_S}|R_{\mu n}|^2|R_{\mu,N_S+l}|^2. \tag{56}$$

For $N_S=1$, this expression should reproduce Eq. (25).

VI. ANALYSIS OF THE EIGENSTATES OF THE SPIN-PHONON SYSTEM

A. Spinness and off-resonance phonon emission

Although the formalism of the preceding section is sufficient to describe the dynamics of the spin-phonon system in terms of transition between different bare (unperturbed) modes, it is also interesting to look closer at the true spin-phonon eigenstates. Throughout this section, we consider phonons as undamped, $L^*_{\mu n}=R_{\mu n}$. The eigenstates are superpositions of spin and phonon states, so the first question would be to determine the fractions of spin and phonon states in any eigenstate, or, as it can be termed, their "spinness" and "phononness." For instance, the spinness of the state μ is defined by

$$\text{spinness}_{\mu}=\sum_{n=1}^{N_S}|R_{\mu n}|^2, \tag{57}$$

while the phononness is defined by a similar expression with summation over phonon indices. Note that spinness enters the expression for the asymptotic spin excitation p_{∞} [Eq. (48)]. Obviously, the sum of spinness and phononness of any state μ is 1. Spinness summed over μ gives the total number of spins. Far from the resonance, the eigenstates are mainly phonon states, so that their spinness is small and can be calculated perturbatively. Labeling these states by the wave vector $\mathbf{k}$ instead of μ, one has $R_{\mathbf{q}k}\cong\delta_{\mathbf{q}k}$, where δ is the Kronecker symbol, and, in the first order of the perturbation theory,

$$R_{\mathbf{k}i}\cong-\frac{1}{\sqrt{N}}\frac{A_{i\mathbf{k}}}{\omega_{\mathbf{k}}-\omega_0}. \tag{58}$$

With this one obtains

$$\text{spinness}_{\mathbf{k}}\cong\frac{n_S|V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}}-\omega_0)^2}\Rightarrow\frac{B}{2}\frac{\Gamma^2}{(\omega_{\mathbf{k}}-\omega_0)^2}. \tag{59}$$

The last expression was obtained for $|V_{\mathbf{k}}|^2=|V|^2$ with the help of Eq. (32). One can see that for a large bottleneck parameter, the interaction of phonons with spins becomes large, so that phonon modes are noticeably hybridized with spins even relatively far from the resonance. This means, dynamically, that the number of phonon modes that exchange excitation with spins is not just a fixed number N_{Γ} determined by the single-spin relaxation rate Γ [see Eq. (27)], and it increases with B. Of course, Eq. (59) becomes inapplicable near the resonance. However, one can figure out its behavior for $B\gg 1$. In this case, the spinness of the states near the resonance should approach 1. One can reproduce this behavior by adding $(B/2)\Gamma^2$ in the denominator of Eq. (59). This is in accordance with Eqs. (34) and (35) that define the number of phonon modes on speaking terms with the spins.

For $B\ll 1$, we will see in numerical results that spinness remains small everywhere including the resonance. This means that initially prepared states with the excitation localized on spins will decompose over the true eigenstates that have a very small fraction of spin states, so that the excitation will migrate completely into the phonon subsystem. To the contrary, for $B\gg 1$, the initially prepared state will decompose over eigenstates that have spinness close to 1, so that the excitation mostly remains on spins. The latter is the phonon bottleneck.

Using Eqs. (58) and (56) allows one to obtain the probability of emission of a phonon with a wave vector $\mathbf{k}$ far from the resonance. With $\mu\Rightarrow\mathbf{q}$, one obtains,

$$n_{\mathbf{k}}=\frac{1}{N_S}\sum_{\mathbf{q}}\sum_{i=1}^{N_S}|R_{\mathbf{q}i}|^2|R_{\mathbf{q}\mathbf{k}}|^2\cong\frac{1}{N_S}\sum_{i=1}^{N_S}|R_{\mathbf{k}i}|^2=\frac{1}{N}\frac{|V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}}-\omega_0)^2}, \tag{60}$$

independently of the bottleneck parameter B and coinciding with Eq. (25) far from the resonance. Independence of this result from B, unlike Eq. (59), is due to the fact that there is only one excitation in the system. With increasing the number of spins and thus B, the probability that this excitation migrates to the phonon subsystem can only decrease, as will be seen in numerical results.

B. Spin-phonon modes

To quantify the spin-phonon hybridization in the general case, one can introduce the average phonon detuning from the spins $\omega_{\mathbf{k}}-\omega_0$ in any eigenstate μ as

$$\langle\omega_{\mathbf{k}}-\omega_0\rangle_{\mu}\equiv\frac{\sum_{\mathbf{k}}|R_{\mu\mathbf{k}}|^2(\omega_{\mathbf{k}}-\omega_0)}{\sum_{\mathbf{k}}|R_{\mu\mathbf{k}}|^2}, \tag{61}$$

where the denominator is the phononness of the eigenstate μ introduced above. Note that this definition does not include the momentum carried by spins. Thus, Eq. (61) principally cannot completely reproduce the results for dense magnetic systems. Plotting the energy (frequency) eigenvalues ω_{μ} vs $\langle\omega_{\mathbf{k}}-\omega_0\rangle_{\mu}$ reveals that near the resonance, there are pairs of two different frequencies Ω_{μ} for the same value of $\langle\omega_{\mathbf{k}}-\omega_0\rangle_{\mu}$. This is the spin-phonon splitting described by Eq (30). Far from the resonance, the relation between

$\langle \omega_{\mathbf{k}} - \omega_0 \rangle_\mu$ and the frequency Ω_μ corresponds to a pure phonon mode.

C. Resonance scattering of phonons

One also can study the admixture of other phonon modes to the given phonon mode because of the phonon scattering on spins. This can be described by the dispersion

$$\delta\{\omega_{\mathbf{k}} - \omega_0\}_\mu \equiv \sqrt{\frac{\sum_{\mathbf{k}} |R_{\mu\mathbf{k}}|^2 (\omega_{\mathbf{k}} - \omega_0 - \langle \omega_{\mathbf{k}} - \omega_0 \rangle_\mu)^2}{\sum_{\mathbf{k}} |R_{\mu\mathbf{k}}|^2}}. \tag{62}$$

Far from the resonance, the eigenstates are almost pure phonons, so that $\delta\{\omega_{\mathbf{k}} - \omega_0\}_\mu$ is small. At resonance, $\delta\{\omega_{\mathbf{k}} - \omega_0\}_\mu$ has a maximum that corresponds to the resonance scattering.

VII. NUMERICAL RESULTS AND ANALYSIS

Here, we study the systems containing a large number of spins diluted so that $k_0 r_0 \gg 1$, where k_0 is the wave vector of a resonant phonon and r_0 is the typical distance between the neighboring spins. In this case, a phonon emitted by one spin has a random phase as it reaches another spin, so that one can replace the factors $e^{-i\mathbf{k}\cdot\mathbf{r}_i}$ in the spin-phonon coupling $A_{i\mathbf{k}}$ [see Eq. (4)] by $e^{-i\varphi}$, where φ is a random number in the interval $(0, 2\pi)$. As a result, in the case of diluted spins, the problem becomes insensitive to the space dimensionality as soon as one replaces the spin-phonon interaction amplitudes $V_{\mathbf{k}}$ by constants V expressed through the one-spin relaxation rate Γ given by Eq. (18).

This has an important implication for numerical calculations. In three- and two-dimensional systems with phonon modes quantized in a box, the phonon density of states $\rho_{\mathrm{ph}}(\omega)$ is a ragged function for the moderately large numbers of phonon modes amenable to computations. To make $\rho_{\mathrm{ph}}(\omega)$ a smooth enough function leading to smooth dependences of physical quantities on parameters, one has to work with millions of phonon modes, which is prohibitive. The fact that the problem for diluted spins becomes insensitive to the space dimensionality allows one to use $1d$ equidistant phonon energy levels that yield a smooth phonon density of states. This dramatically improves the quality of numerical results. (Of course, using a realistic $3d$ phonon model with explicit phase factors $e^{-i\mathbf{k}\cdot\mathbf{r}_i}$ yields essentially the same results, however with a larger numerical scatter.)

In the numerical simulations, the absolute values of the spin-phonon matrix elements are set to a unique constant. If not stated explicitly, the phonons are considered as undamped. To reduce the size of the problem, only the phonon modes sufficiently close to the resonance (i.e., within a set detuning tolerance)

$$|\omega_{\mathbf{k}} - \omega_0| \lesssim \Gamma \times \text{detuning tolerance} \tag{63}$$

have been taken into account, while all strongly nonresonant phonon modes have been dropped. In most simulations, detuning tolerance varied between 30 for $B \lesssim 1$ and 150 for $B = 100$. Equation (26) suggests that it would be sufficient to have detuning tolerance of about 3. However, one can see from Eq. (24) that at short times, $\Gamma t \lesssim 1$, the number of the phonon modes responding to the spin is much larger than that at asymptotically large times. Thus, choosing an insufficiently large detuning tolerance leads to loss of precision at short times. Also for $B \gtrsim 1$, the number of relevant phonon modes becomes large [see Eqs. (35) and (34)], which requires large detuning tolerance (DT).

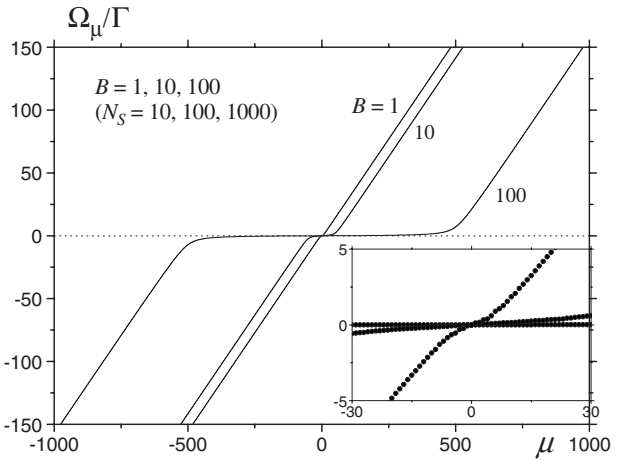

FIG. 1. Frequency eigenvalues Ω_μ plotted vs their appropriately shifted number for different values of the bottleneck parameter B.

The number of phonon modes N_{DT} within the detuning-tolerance interval is given by $N_{\mathrm{DT}} = N\rho_{\mathrm{ph}}(\omega_0) \times 2\Gamma \times$ detuning tolerance. Using this relation, one can eliminate the irrelevant total number of phonon modes N from Eq. (28) and obtain the relation

$$B = \frac{2N_S}{\pi N_{\mathrm{DT}}} \times \text{detuning tolerance}, \tag{64}$$

which was used for the parametrization of simulations. The total number of spins and phonon modes in simulations $N_S + N_{\mathrm{DT}}$ reached the values of about 5000, which is sufficient to attain the thermodynamic limit.

A. Analysis of the eigenstates of the spin-phonon system

Figure 1 shows the frequency eigenvalues Ω_μ plotted vs their number for different values of the bottleneck parameter B. We kept the number of phonon modes within the detuning-tolerance interval of 150 equal to 956, and diagonalized the dynamical matrix Φ for $N_S = 10$, 100, and 1000 that corresponds to $B = 1$, 10, and 100. One can see that for a large number of spins, many states have $\Omega_\mu \cong 0$. These are mostly spin states slightly hybridized with phonons. The density of states of the whole system becomes large near the resonance. There is no gap in the spin-phonon spectrum, contrary to the finding of Refs. 13 and 14. The absence of the gap is the consequence of the rotating-wave approximation made here. For a small number of spins, the spectrum resembles the phonon spectrum. Its distortion due to spins for $B = 1$ can be seen only in the inset.

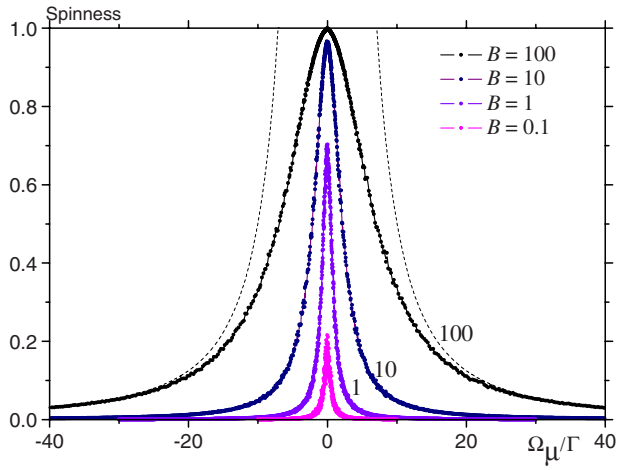

FIG. 2. (Color online) Spinness of the spin-phonon eigenstates vs Ω_μ for different values of B.

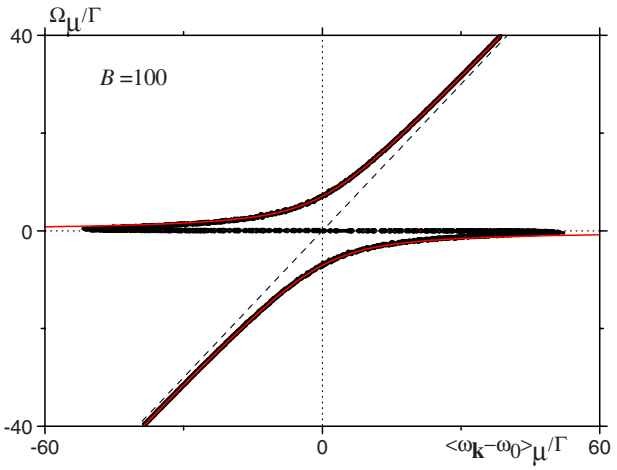

FIG. 3. (Color online) Spin-phonon eigenstates Ω_μ vs the average phonon detuning $\langle\omega_{\mathbf{k}}-\omega_0\rangle_\mu$ that shows splitting of the spin-phonon eigenstates. The solid red line is the result of Eq. (30).

The spinness of the spin-phonon eigenstates [Eq. (57)] is shown in Fig. 2 vs Ω_μ. While for small B the spinness is small everywhere, with a maximum at $\Omega_\mu=0$, for large B the spinness reaches 1 near the resonance. (Note that there are a lot of states with $\Omega_\mu\cong 0$ for $B\gg 1$. The spinness plotted vs the eigenvalue number μ has a wide flat maximum with spinness$_\mu\cong 1$ in this case.) The dashed lines of Eq. (59) drawn for $B=100$ well approximate the spinness far from the resonance, where Ω_μ practically coincides with the unperturbed $\omega_{\mathbf{k}}-\omega_0$. The Lorentzian form

$$\text{spinness}_\mu = \frac{(B/2)\Gamma^2}{\Omega_\mu^2 + (B/2)\Gamma^2} \tag{65}$$

perfectly approximates the results for $B=100$ in the whole region, which could be an indication of an exact solution for $B\gg 1$ that could not be easily found, however. These results, as well as Eq. (59), show that the number of phonon modes that are on speaking terms with spins grows with the concentration of the latter.

Plotting different quantities vs the average phonon detuning $\langle\omega_{\mathbf{k}}-\omega_0\rangle_\mu$ in the eigenstate μ defined by Eq. (61) reveals finer details of the spin-phonon eigenstates. One can see an avoided level crossing of spins and phonons in Fig. 3 that shows Ω_μ vs $\langle\omega_{\mathbf{k}}-\omega_0\rangle_\mu$ for $B=100$. Most of the points in Fig. 3 fall onto the curve described by Eq. (30). Note that the horizontal branches of the spin-phonon spectrum in Fig. 3 do not go infinitely to the left and right, but turn back to the center, so that the numerical points make a continuous curve. This is because Eq. (61) does not take into account the contribution of diluted spins into the momentum. In Fig. 4 (cf. Fig. 2), one can see how both spin-phonon branches gradually change from pure phonon modes to pure spin modes.

The phonon dispersion $\delta\{\omega_{\mathbf{k}}-\omega_0\}_\mu$ defined by Eq. (62) and shown in Fig. 5 for $B=100$ behaves in an especially interesting way. Far from the resonance, it is small but noticeable, which means that phonons are scattering on spins. At resonance, $\langle\omega_{\mathbf{k}}-\omega_0\rangle_\mu=0$, it has a maximum corresponding to the resonance scattering of phonons. In fact, there are two superimposed maxima corresponding to the two split spin-phonon states in Fig. 3. The horizontal joining region in Fig. 3 creates a downward loop in Fig. 5.

B. Dynamics of the spin population

The relaxation of spin excitation $p(t)$ obtained from Eq. (45) (incoherent initial condition) is shown in Fig. 6 for different values of the bottleneck parameter B. The height of the asymptotic bottleneck plateau p_∞ grows with B and tends to 1 as $B\to\infty$. Before reaching the plateau, $p(t)$ performs strongly damped oscillations that manifest the importance of memory effects in the PB problem. The frequency of oscillations is determined by the spin-phonon gap Δ of Eq. (31) that increases with the concentration of spins n_S and thus B.

The bottleneck plateau p_∞ obtained in the case of undamped phonons from Eq. (48) is shown in Fig. 7 vs the

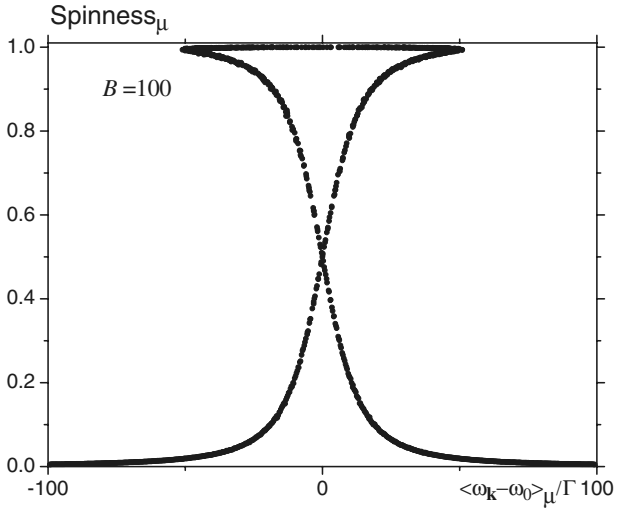

FIG. 4. Spinness vs the average phonon detuning $\langle\omega_{\mathbf{k}}-\omega_0\rangle_\mu$ that shows how both spin-phonon branches gradually change from pure phonon modes to pure spin modes.

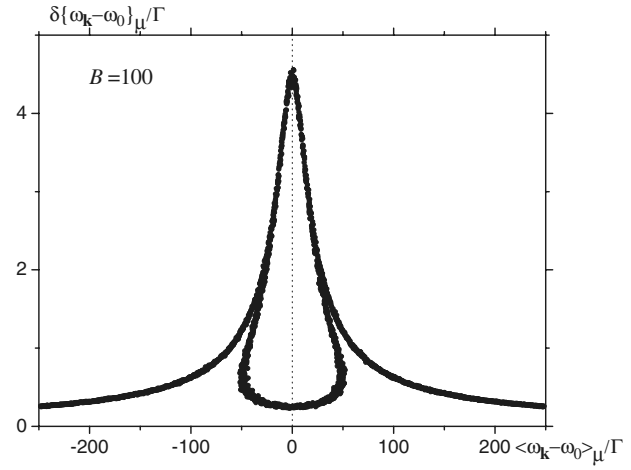

FIG. 5. Phonon dispersion of Eq. (62) showing the resonance phonon scattering on spins.

ratio $N_S/(N_S+N_\Gamma)=B/(1+B)$. Both small- and large-$B$ data can be well fitted with the asymptotes of Eq. (37).

Figure 8 shows the spin relaxation in the case of damped phonons for $B=10$. Although $p(t)$ relaxes to zero for any value of the *ad hoc* phonon damping $\Gamma_{\rm ph}$, the effective spin relaxation rate is much smaller than $\Gamma_{\rm ph}$ for $B\gg 1$. Only in the limit $\Gamma_{\rm ph}\to\infty$, the single-spin relaxation curve of Eq. (22) is recovered. One can see from the curve with $\Gamma_{\rm ph}$ that the spin relaxation via the phonon relaxation in the case of strong bottleneck is nonexponential, as commented upon after Eq. (49). The logarithmic plot in Fig. 9 for $\Gamma_{\rm ph}=10\Gamma$ and $B=300$ shows that the spin relaxation is described by a combination of many exponentials, but there is the dominant slowest exponential at large times. This exponential is even slower than the result of Ref. 11, $p(t)\exp(-\tilde{\Gamma}t)$ with $\tilde{\Gamma}=\Gamma_{\rm ph}/\sqrt{2B}$.

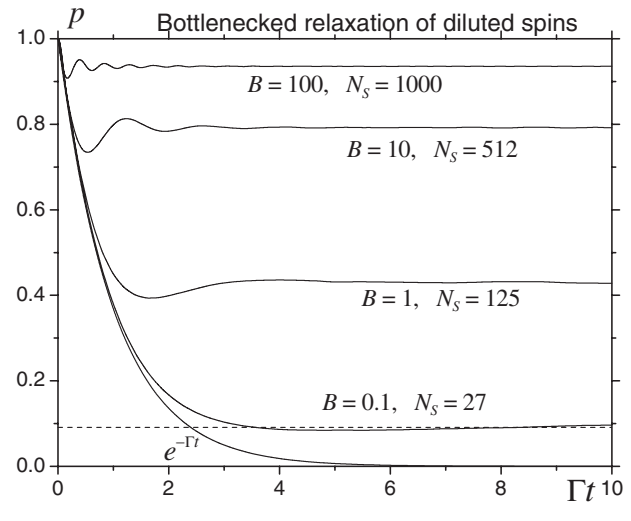

FIG. 6. Bottlenecked relaxation of the spin excitation for different values of the bottleneck parameter B. The number of spins used in simulations are indicated, and the number of phonon modes were chosen appropriately. The dashed horizontal line is the large-time asymptote for $B=0.1$.

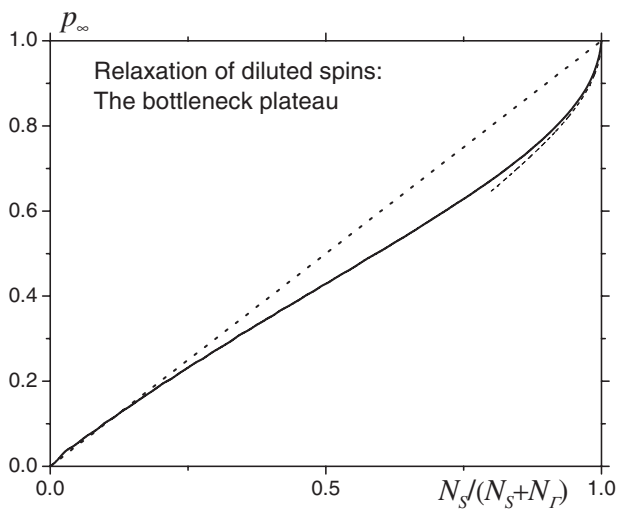

FIG. 7. Bottleneck plateau p_∞ vs $N_S/(N_S+N_\Gamma)=B/(1+B)$. The asymptote $p_\infty=1-1/\sqrt{2B}$ for $B\gg 1$ is shown by the dashed line.

C. Emitted phonons in the final state

Distribution of the emitted phonons in the final state (in the case $\Gamma_{\rm ph}=0$) found from Eq. (56) is shown in Fig. 10(a). The total number of emitted phonons following Eq. (8) is equal to $1-p_\infty$ and decreases with increasing the bottleneck parameter B, which is seen in the figure. The wings of the line of emitted phonons do not depend on B, according to Eq. (60), whereas the central part of the line is suppressed with B. As a result, the linewidth of the emitted phonons broadens with increasing B.

As argued above, the present method formally considering a single excitation shared by the spin and phonon subsystems, in fact, is valid in any practical situation where the system is weakly excited, although the number of excitations can be macroscopically large. In this situation, increasing the number of spins (and thus B) means increase of the excitation that is partially transferred to the phonon subsystem. This is to say that in real situations, B and the number of emitted phonons are not inversely related as in the case of a

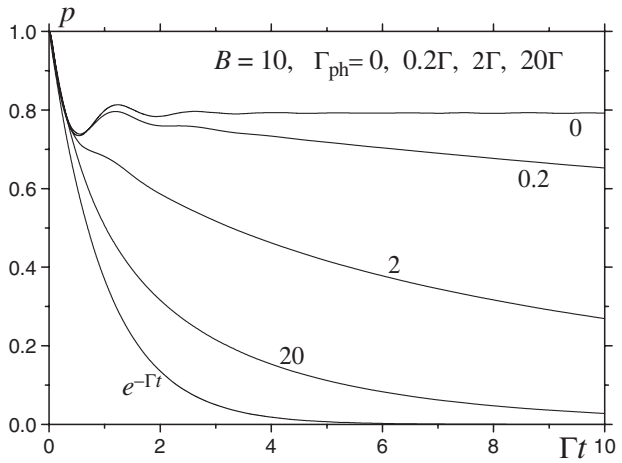

FIG. 8. Bottlenecked relaxation of the spin excitation for $B=10$ and different values of the *ad hoc* phonon damping $\Gamma_{\rm ph}$.

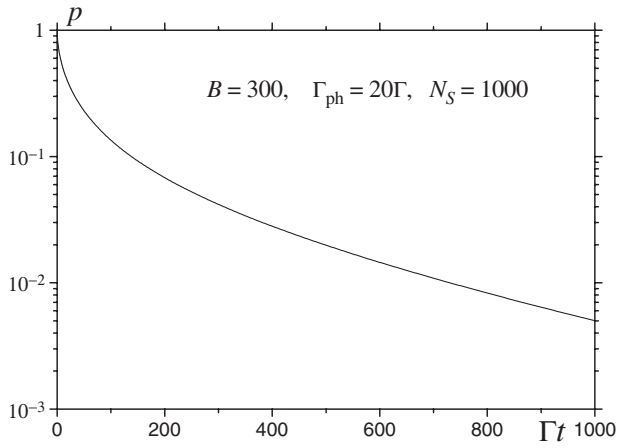

FIG. 9. Nonexponential relaxation of the spin excitation for $B=300$ and $\Gamma_{\mathrm{ph}}=10\Gamma$ in logarithmic scale.

single excitation. Thus, it makes sense to represent the number of emitted phonons in the normalized form as in Fig. 10(b) to make the phonon line shape for large B better visible.

The numerical results for $B \gg 1$ can be perfectly fitted by

$$n_{\mathbf{k}} = \frac{1}{\pi N \rho_{\mathrm{ph}}(\omega_0)} \frac{\Gamma/2}{(\omega_{\mathbf{k}} - \omega_0)^2 + 2B\Gamma^2}, \tag{66}$$

which is a particular form of

$$n_{\mathbf{k}} = \frac{1}{N} \frac{|V_{\mathbf{k}}|^2}{(\omega_{\mathbf{k}} - \omega_0)^2 + \Delta_{\mathbf{k}}^2}, \tag{67}$$

with the spin-phonon gap $\Delta_{\mathbf{k}}$ given by Eq. (31). Equations (66) and (67) should be compared with Eqs. (26) and (25).

VIII. INHOMOGENEOUS BROADENING OF SPIN LEVELS

In some systems, the inhomogeneous broadening defined by Eq. (3) is much larger than the natural spin linewidth Γ or the spin-phonon splitting Δ. The number of spins within the frequency interval $d\omega_0$ around the frequency ω_0 is

$$dN_S = N_S \rho_S(\omega_0) d\omega_0, \tag{68}$$

where the spin density of states $\rho_S(\omega_0)$ satisfies $\int_0^\infty \rho_S(\omega_0) d\omega_0 = 1$. An example is the Gaussian line shape

$$\rho_S(\omega_0) = \frac{1}{\sqrt{2\pi}\delta\omega_0} \exp\left[-\frac{(\omega_0 - \overline{\omega_0})^2}{2(\delta\omega_0)^2} \right]. \tag{69}$$

In the presence of a large inhomogeneous broadening, the number of phonons on speaking terms with spins can be estimated as $N_{\delta\omega_0} \sim N\pi\rho_{\mathrm{ph}}(\omega_0)\delta\omega_0$, which should replace N_Γ of Eq. (27) in the definition of the bottleneck parameter B that becomes smaller than for the pure model by a factor of $\delta\omega_0/\Gamma \gg 1$. Consideration of this kind can be found in Van Vleck's original paper[2] and subsequent publications. In fact, as we shall see below in this section, the relation between the numbers of spins and phonon modes that can exchange excitation is different in different frequency regions within the inhomogeneous spin linewidth $\delta\omega_0$ and a frequency-resolved description of the phonon bottleneck is possible.

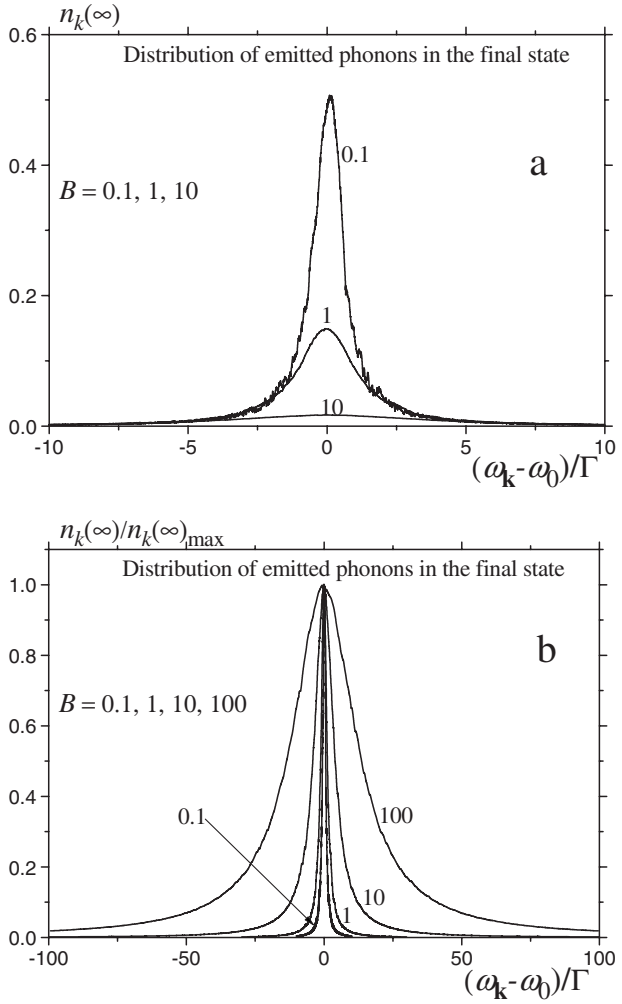

FIG. 10. Distribution of emitted phonons in the final state for different values of B: (a) in natural units; (b) normalized.

In simulations, the macroscopic limit is achieved if the average distance between the neighboring spin levels becomes smaller than the natural linewidth Γ

$$\frac{1}{N_S \rho_S(\omega_0)} \ll \Gamma \tag{70}$$

[cf. Eq. (29)]. Since both of these conditions should be satisfied, both N and N_S should be large enough. The results for the bottleneck plateau p_∞ vs the inhomogeneous broadening $\delta\omega_0$ in Eq. (69), obtained numerically from Eq. (48), are shown in Fig. 11. Since the number of phonons that can exchange energy with spins increases with $\delta\omega_0$, the bottleneck plateau p_∞ decreases. For $B \lesssim 1$, the most pronounced decrease occurs at $\delta\omega_0 \sim \Gamma$, the crossover from the natural linewidth to the inhomogeneous linewidth. In the case $B \gg 1$, this crossover occurs at $\delta\omega_0 \sim \sqrt{B}\Gamma \sim \Delta$, in accordance with the comments after Eq. (59).

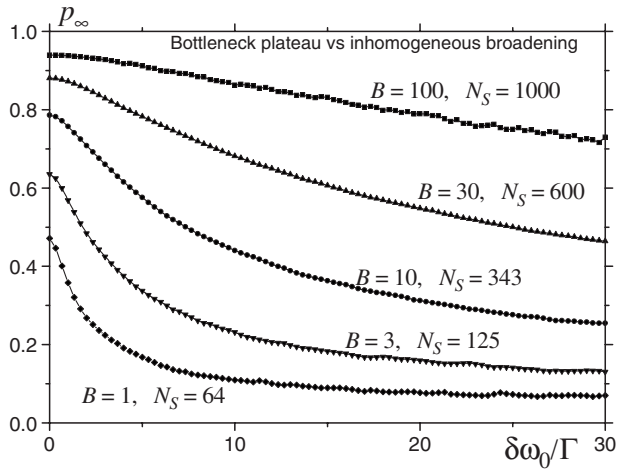

FIG. 11. The bottleneck plateau in the case of inhomogeneous broadening with the Gaussian line shape vs $\delta\omega_0$.

Clearly, for $\delta\omega_0 \gg \Gamma, \Delta$, much more phonons can exchange their energy with spins, so that the bottleneck condition is alleviated and spin relaxation is facilitated. In this case, the problems simplified since spins and phonons exchange energy only within the frequency interval of order $\max(\Gamma, \Delta)$, which is much narrower than the inhomogeneous linewidth $\delta\omega_0$. Thus, one can split the latter into the frequency intervals $\Delta\omega_0$ around ω_0 that satisfy $\max(\Gamma, \Delta) \ll \Delta\omega_0 \ll \delta\omega_0$, and consider the energy exchange between spins and phonons in each of these intervals independently. The spin and phonon densities of states within each interval $\Delta\omega_0$ can be considered as constants, and they define the bottleneck parameter in a frequency interval around ω_0

$$B_{\omega_0} \equiv \frac{N_S}{N}\frac{\rho_S(\omega_0)}{\rho_{\rm ph}(\omega_0)} = n_S\frac{\rho_S(\omega_0)}{\rho_{\rm ph}(\omega_0)}. \tag{71}$$

Since the phonon density of states is a smooth function, one can replace $\rho(\omega_0) \Rightarrow \rho(\overline{\omega_0})$. On the other hand, $\rho_S(\omega_0)$ and thus B_{ω_0} have a maximum at $\omega_0 = \overline{\omega_0}$. One can parametrize

$$B_{\omega_0} = \frac{\rho_S(\omega_0)}{\rho_S(\overline{\omega_0})}B_{\overline{\omega_0}}, \tag{72}$$

where $B_{\overline{\omega_0}}$ is the bottleneck parameter at the center of the line. For a Gaussian line shape of Eq. (69), one has

$$B_{\overline{\omega_0}} = \frac{n_S}{\sqrt{2\pi}\rho_{\rm ph}(\omega_0)\,\delta\omega_0}. \tag{73}$$

The spin excitation reaches a frequency-dependent plateau $p_\infty(\omega_0)$ that depends on B_{ω_0}. The average over the spin line shape $\rho_S(\omega_0)$ of Eq. (68) now becomes

$$\overline{p_\infty} = \int_0^\infty d\omega_0 \rho_S(\omega_0) p_\infty(\omega_0). \tag{74}$$

Evidently, $\overline{p_\infty} < p_\infty(\overline{\omega_0})$ since the bottleneck effect weakens away from the center of the spin band. The numerically found dependence of $p_\infty(\omega_0)$ is very close to

$$p_\infty(\omega_0) = \frac{B_{\omega_0}}{1 + B_{\omega_0}}, \tag{75}$$

which can be expected from general statistical arguments. This important formula will be used below to obtain results for the bottleneck plateau taking into account the inhomogeneously broadened spin line shape. The illustrations will be done for the Gaussian line shape of Eq. (69).

In the case $B_{\overline{\omega_0}} \ll 1$, one obtains

$$\overline{p_\infty} \cong B_{\overline{\omega_0}} \int_0^\infty d\omega_0 \frac{[\rho_S(\omega_0)]^2}{\rho_S(\overline{\omega_0})} \tag{76}$$

that with the help of Eq. (69) yields

$$\overline{p_\infty} \cong B_{\overline{\omega_0}}/\sqrt{2}. \tag{77}$$

If $B_{\overline{\omega_0}} \gg 1$, one can use

$$\overline{p_\infty} = 1 - \int_0^\infty d\omega_0 \frac{\rho_S(\omega_0)}{1 + B_{\omega_0}}, \tag{78}$$

which follows from Eq. (75). The integrand of this expression is close to $\rho_S(\overline{\omega_0})/B_{\overline{\omega_0}} = \text{const}$ for $B_{\omega_0} \gtrsim 1$, and it decays abruptly further from the center of the spin line where $B_{\omega_0} \lesssim 1$. Let us define ω^* that satisfies $B_{\omega^*} = 1$, that is, $\rho_S(\omega^*) = \rho_S(\overline{\omega_0})/B_{\overline{\omega_0}}$. Then, from Eq. (78), one obtains, approximately,

$$\overline{p_\infty} \cong 1 - \frac{2\delta\omega^*\rho_S(\overline{\omega_0})}{B_{\overline{\omega_0}}}, \tag{79}$$

where $\delta\omega^* \equiv |\omega^* - \overline{\omega_0}|$. For the Gaussian line shape of Eq. (69), one has $\delta\omega^* = \delta\omega_0\sqrt{2\ln B_{\overline{\omega_0}}}$ and, finally,

$$\overline{p_\infty} \cong 1 - \frac{2}{B_{\overline{\omega_0}}}\sqrt{\frac{\ln B_{\overline{\omega_0}}}{\pi}}, \quad B_{\overline{\omega_0}} \gg 1. \tag{80}$$

Figure 12 shows $\overline{p_\infty}$ in the whole interval of $B_{\overline{\omega_0}}$ calculated numerically from Eqs. (69), (74), (75), and (72).

Next we calculated the time dependence of the spin excitation $p(t)$ for spins within a frequency interval $\Delta\omega_0$ around ω_0 that satisfies $\max(\Gamma, \Delta) \ll \Delta\omega_0 \ll \delta\omega_0$, as explained above. Again, the incoherent initial condition for spins leading to Eq. (48) was used. Only spins and phonon modes within the interval $\Delta\omega_0$ were taken into account, while all other spins and phonon modes have been ignored. This allowed us to greatly reduce the computation time. The results have been shown to be practically independent of $\Delta\omega_0$ as long as the condition $\Gamma \ll \Delta\omega_0$ is fulfilled. The distribution of spin frequencies within $\Delta\omega_0$ was taken to be equidistant (similar to the phonon modes), which allowed us to eliminate statistical scattering. In this realization of the model, spins and phonon modes form two equivalent groups interacting with each other. The results of computations for undamped phonons are shown in Fig. 13. Note that here oscillations visible in Fig. 6 are completely washed out. The asymptotic values of p are in

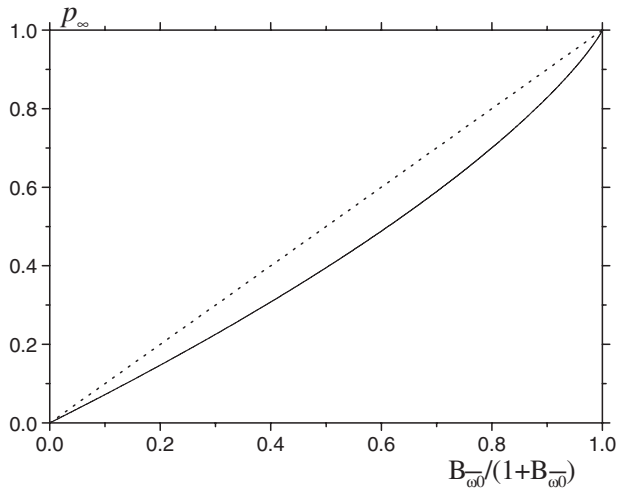

FIG. 12. The bottleneck plateau in the case of strong ($\delta\omega_0 \gg \Gamma, \Delta$) inhomogeneous broadening with the Gaussian line shape vs the bottleneck parameter B_{ω_0}.

accord with Eq. (75). Having the results for $p(t)$ for any ω_0, one could now perform integration over spin frequencies ω_0 similar to Eq. (74) using, e.g., Eq. (69).

One can compare the results of the present calculation within the frequency interval $\Delta\omega_0$ with the results of the earlier general calculation shown in Fig. 11. The connection is provided by the identity

$$B_{\overline{\omega_0}} = \sqrt{\frac{\pi}{2}}\frac{\Gamma}{\delta\omega_0}B \tag{81}$$

that follows from Eqs. (28), (71), and (69). For instance, the rightmost point of the curve $B=1$ in Fig. 11 is $p_\infty \simeq 0.070$ for $\delta\omega_0/\Gamma = 30$. Equation (81) yields then $B_{\overline{\omega_0}} \simeq 0.0418$. For such small $B_{\overline{\omega_0}}$, one can use Eq. (77) that yields $p_\infty \simeq 0.030$. The disagreement with the value $p_\infty \simeq 0.070$ can be explained by

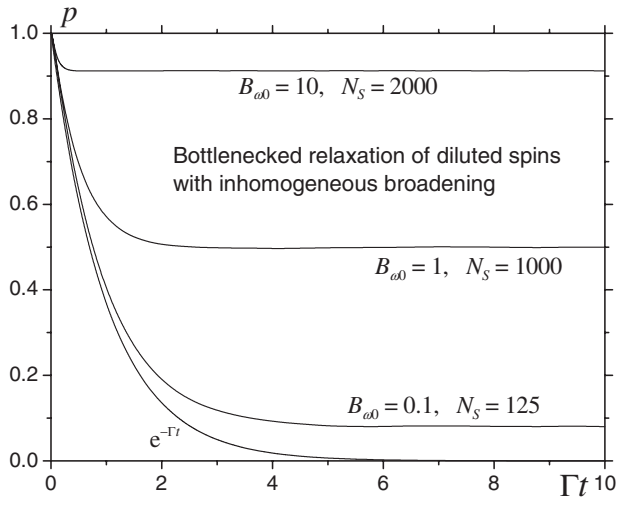

FIG. 13. Time dependence of the spin excitation $p(t)$ for the spins with frequencies around ω_0 in the case of strong inhomogeneous broadening.

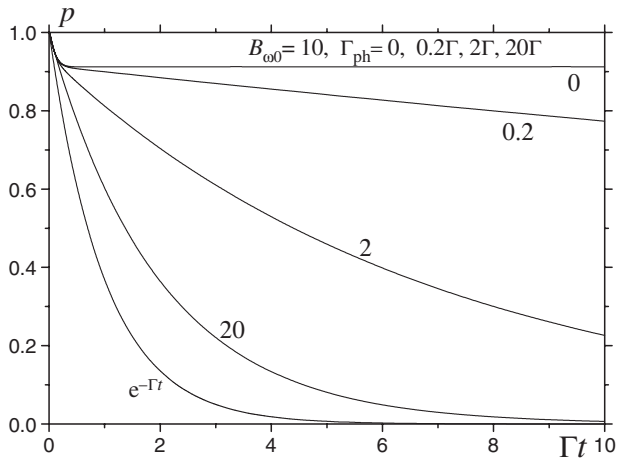

FIG. 14. The same in the case of damped phonons. Again, for $B \gg 1$, the effective spin relaxation rate is much smaller than the phonon relaxation rate Γ_{ph}.

the fact that the number of spins $N_S = 64$ in the general calculation for $B=1$ is too small to reach the asymptotic result given by Eq. (75) and statistical scattering is still substantial. For the rightmost point of the curve $B=3$ in Fig. 11, the disagreement between the results of the two calculations is smaller.

The results for spin relaxation in the case of damped phonons are shown in Fig. 14. One can see that for $B \gg 1$, the effective spin relaxation rate is much smaller than the phonon relaxation rate Γ_{ph}, similar to the case without inhomogeneous broadening (see Fig. 8).

IX. IMPLEMENTATION FOR MOLECULAR MAGNETS

Let us work out the general expressions and estimate the parameters that govern the bottlenecked spin relaxation for molecular magnets, in particular, for the most popular compound Mn_{12}. Historically, the phonon bottleneck was first observed in other systems. However, there is an experimental evidence of the phonon bottleneck in molecular magnets as well. On the other hand, molecular magnets are especially convenient because of the universal form of the spin-phonon relaxation that does not depend on any unknown spin-phonon coupling constants.[15] The spin relaxation between the adjacent levels of the uniaxial spin Hamiltonian $-DS_z^2$ is due to the rotation of the crystallographic easy axis by the transverse phonons. The rate of decay from the first excited state $|-S+1\rangle$ to the ground state $|-S\rangle$ is given by the formula

$$\Gamma = \frac{S(2S-1)^2 D^2 \omega_0^3}{12\pi\hbar\rho v_t^5}, \tag{82}$$

where ρ is the mass density and v_t is the speed of transverse phonons. The most recent derivation of this formula for the transitions between any adjacent spin levels can be found in Appendix A of Ref. 16. In zero field, one has $\hbar\omega_0 = E_{-S+1} - E_{-S} = (2S-1)D$ and Eq. (82) can be cast into the elegant form

$$\Gamma = \frac{S}{12\pi}\frac{\omega_0^5}{\Omega_t^4}, \quad \Omega_t \equiv \left(\frac{\rho v_t^5}{\hbar}\right)^{1/4}, \tag{83}$$

where Ω_t is the characteristic frequency of spin-phonon interaction related to the similar energy $\mathcal{E}_t$ of Ref. 17 by $\hbar\Omega_t = \mathcal{E}_t$. The phonon density of states of Eq. (20), multiplied by 2, the number of transverse phonon modes, has the form

$$\rho_{\rm ph}(\omega_0) = \frac{1}{\pi^2}\frac{\omega_0^2}{\tilde{\Omega}_D^3}, \quad \tilde{\Omega}_D \equiv \frac{v_t}{v_0^{1/3}}, \tag{84}$$

where v_0 is the unit-cell volume. The frequency $\tilde{\Omega}_D$ is related to the Debye frequency Ω_D as $\Omega_D = (6\pi^2)^{1/3}\tilde{\Omega}_D$. Thus, the bottleneck parameter B of Eq. (28) becomes

$$B = \frac{12\pi^2}{S}\frac{\Omega_t^4\tilde{\Omega}_D^3}{\omega_0^7}n_S. \tag{85}$$

For Mn_{12}, one has $S=10$, $\rho = 1.83$ g/cm^3, and $v_0 = 3716$ Å^3, and, from the heat-capacity measurements,[18] follows $\hbar\Omega_D/k_B \simeq 38$ K, thus $\hbar\tilde{\Omega}_D/k_B \simeq 10$ K. Further, one obtains $v_t \simeq 2\times 10^3$ m/s and $\hbar\Omega_t/k_B \simeq 210$ K, whereas $\hbar\omega_0/k_B \simeq 12$ K. Plugging these parameters into Eq. (85), one obtains $B \simeq 5\times 10^5 n_S$. This means that for a undiluted Mn_{12} crystal, $n_S = 1$, the bottleneck parameter is huge.

Of course, for undiluted magnetic crystals, the physics includes the effects of coherence and it is more complicated than just the phonon bottleneck. The pure bottleneck situation is realized for a sufficient dilution, so that $k_0 r_0 \gtrsim 2\pi$ and the phases of emitted and reabsorbed phonons can be considered as random. Using $r_0 = (v_0/n_S)^{1/3}$ for the average distance between the neighboring magnetic molecules and $k_0 = \omega_0/v_t$, one can rewrite the condition of sufficient dilution as

$$n_S \lesssim n_S^* \equiv \left(\frac{\omega_0}{2\pi\tilde{\Omega}_D}\right)^3. \tag{86}$$

We call n_S^* critical concentration or critical dilution. With the parameters above, one obtains $n_S^* \simeq 0.008$. Even at this dilution, the bottleneck parameter remains huge,

$$B^* \equiv \frac{12\pi^2}{S}\frac{\Omega_t^4\tilde{\Omega}_D^3}{\omega_0^7}n_S^* = \frac{3}{2\pi S}\left(\frac{\Omega_t}{\omega_0}\right)^4, \tag{87}$$

which numerically yields $B^* \simeq 4000$. Note that for spin transitions between excited levels, the energy differences $\hbar\omega_0 = E_{m+1} - E_m = -(2m+1)D$ are smaller than above, thus the values of B are even larger.

Now from Eq. (19), one obtains the estimation of the spin-phonon matrix element

$$|V|^2 = \frac{\Gamma}{2\pi\rho_{\rm ph}(\omega_0)} = \frac{S}{24}\frac{\omega_0^3\tilde{\Omega}_D^3}{\Omega_t^4} \tag{88}$$

(which also could be obtained directly). This yields the spin-phonon splitting of Eq. (31) in the form

$$\Delta = \sqrt{n_S}\sqrt{\frac{S}{6}\frac{\omega_0^3\tilde{\Omega}_D^3}{\Omega_t^4}} \tag{89}$$

and

$$\Delta^* = \sqrt{n_S^*}\sqrt{\frac{S}{6}\frac{\omega_0^3\tilde{\Omega}_D^3}{\Omega_t^4}} = \sqrt{\frac{S}{6}}\frac{1}{(2\pi)^{3/2}}\frac{\omega_0^3}{\Omega_t^2}. \tag{90}$$

Numerically, one obtains $\hbar\Delta/k_B \simeq 40\sqrt{n_S}$ mK and $\hbar\Delta^*/k_B \simeq 3.6$ mK.

Let us now discuss the role of inhomogeneous broadening (IB) on the phonon bottleneck in molecular magnets. First, there is the dipole-dipole interaction (DDI) that is as strong as about $E_{DDI}/k_B \simeq 67$ mK between the two neighboring Mn_{12} molecules. This would result in the change of the spin transition frequency for adjacent spin levels by $(E_{DDI}/k_B)/S \simeq 6.7$ mK. Sometimes, for simplicity, the DDI is considered as a kind of IB. This is an oversimplification, at least for weakly excited states considered here. Rigorous treatment of the Landau-Zener effect at fast sweep with an account of both DDI and true IB (random hyperfine fields[19]) shows that these two effects compete with each other, rather than simply add. In the present case, the magnetostatic field smoothly varies along the crystal (if the crystal shape is non-elliptic), so that its change on the unit-cell distance is very small. Thus, the DDI as a source of IB will be neglected.

A larger source of inhomogeneous broadening in Mn_{12} is the hyperfine interaction with their own $N_I = 12$ nuclear spins $I = 5/2$. With the hyperfine coupling A between the total electronic spin S and each of the nuclear spins I of $A/k_B = 2$ mK,[20] the dispersion of the hyperfine field (HF) δH_{HF} on the electronic spin is given by[15,21]

$$\delta H_{HF} = \frac{\sqrt{\sigma_I}A}{g\mu_B}, \quad \sigma_I = \frac{N_I}{3}I(I+1), \tag{91}$$

whereas the inhomogeneous line shape is Gaussian. Numerically, one obtains $\delta H_{HF} \simeq 8.8$ mT. For the transition between adjacent spin levels for the inhomogeneous broadening $\delta\omega_0$ in Eq. (69), one has $\hbar\delta\omega_0 = g\mu_B\delta H_{HF}$, thus $\hbar\delta\omega_0/k_B \simeq 12$ mK. In another popular compound Fe_8, the IB is mainly due to the DDI with nuclear spins of hydrogen atoms present in magnetic molecules, $\delta H \simeq 0.8$ mT according to Ref. 22.

The greatest source of IB is, however, the dispersion of the uniaxial anisotropy D (the so-called D strain), which can be due to strains created by dislocations[23,24] or, more likely, due to chemical disorder in ligands surrounding magnetic atoms.[25] The electron paramagnetic resonance linewidth of the transition $9 \leftrightarrow 10$ in Mn_{12} is about 200 mT,[26,27] which suggests Gaussian dispersion $\delta D \simeq 0.02D$.[27–29] In Fe_8, the relative dispersion is smaller: $\delta D \simeq 0.01D$.[27] Similar is the case for another molecular magnet Ni_4: $\delta D \simeq (0.005-0.01)D$ in good crystals.[30] The inhomogeneous

linewidth of 200 mT exceeds the spin-phonon splitting Δ of Eq. (89) by far, so that the latter cannot emerge in molecular magnets.

An important question is what happens with IB upon dilution. It was shown[31] that a particular member of the Mn_{12} family remains stable upon dilution and retains its undiluted value of $\delta D/D$. This contrasts the data obtained for other Mn_{12} derivatives (see, e.g., Ref. 32 and citations in Ref. 31). Recent experiments on Ni_4 show a large D strain in diluted samples: $\delta D \simeq 0.11D$.[33]

In the case of strong inhomogeneous broadening $\delta\omega_0 \gg \Gamma, \Delta$ that is realized in molecular magnets, the relaxation is governed by the frequency-interval bottleneck parameter $B_{\overline{\omega_0}}$ of Eq. (73). With the help of Eq. (84), identifying $\omega_0 = \overline{\omega_0}$, one obtains

$$B_{\overline{\omega_0}} = \frac{n_S}{\sqrt{2\pi}} \frac{\pi^2 \tilde{\Omega}_D^3}{\overline{\omega_0}^2 \delta\omega_0}. \tag{92}$$

At critical dilution, this becomes

$$B^*_{\overline{\omega_0}} = \frac{n_S^*}{\sqrt{2\pi}} \frac{\pi^2 \tilde{\Omega}_D^3}{\overline{\omega_0}^2 \delta\omega_0} = \frac{1}{2^{7/2}\pi^{3/2}} \frac{\overline{\omega_0}}{\delta\omega_0} \simeq 0.016 \frac{\overline{\omega_0}}{\delta\omega_0}. \tag{93}$$

For the dominating D-strain mechanism, this amounts to

$$B^*_{\overline{\omega_0}} \simeq 0.016 \frac{D}{\delta D}. \tag{94}$$

With $\delta D \simeq 0.02D$ for Mn_{12}, one obtains $B_{\overline{\omega_0}} \simeq 100 n_S$, whereas $n_S^* \simeq 0.008$, so that $B^*_{\overline{\omega_0}} \simeq 0.8$. In this case, Eq. (80) yields $p_\infty \simeq 0.44$ for the bottleneck plateau, which is still quite a big value that requires phonon damping to be taken into account to ensure a complete relaxation.

Of course, collective effects in spin-phonon relaxation should be much stronger for undiluted crystals, $n_S = 1$. Corresponding analysis will be done elsewhere.

X. DISCUSSION

The problem of the phonon bottleneck considered in this paper in the weak-excitation limit is only a part of a larger problem of collective spin-phonon relaxation. The bottleneck in the pure form occurs for magnetically diluted systems that satisfy the condition $k_0 r_0 \gg 1$, where k_0 is the wave vector of a resonant phonon and r_0 is the typical distance between the neighboring spins. If this condition is violated, one cannot consider the phases of emitted phonons reaching other spins as random, and the interference effects become important. The well-known example of interference effects is superradiance[3,12] that requires, among other conditions, a coherent initial condition of spins. In contrast to the bottleneck, superradiance dramatically increases the relaxation rate, so that the two effects should compete. On the other hand, destructive interference effects in the case of incoherent initial condition or dynamical loss of coherence due to the inhomogeneous broadening can lead to suppression of relaxation that resembles the PB, but has a different physical origin. For this reason, using the results of this paper to interpret experiments should be done with care as the experimental observations can be a mixture of different effects. In particular, the results obtained in this paper are not applicable to undiluted molecular magnets.

Considering the weak-excitation limit in this paper allowed us to drastically simplify the Schrödinger equation and obtain numerically exact results for the PB effect with and without inhomogeneous broadening of spins and phonon damping. It was confirmed that the bottleneck parameter B quantifying the statistical weights of spins and resonant phonons, introduced in Ref. 11, plays the main role in the problem. Fundamentally, the most interesting case corresponds to the pure model without inhomogeneous spin broadening and phonon damping. For this model, similar to the results of Ref. 11, the spin excitation $p(t)$ was shown to oscillate upon approaching the bottleneck plateau (see Fig. 6). However, these oscillations have a smaller amplitude and are more strongly damped than the analytical results of Ref. 11. The frequency of these oscillations corresponds to the gap Δ between the two branches of the hybridized magnetoelastic waves at resonance [see Eq. (30) and Fig. 3].

It was shown that the bottleneck parameter effectively decreases in the presence of inhomogeneous broadening that alleviates the bottleneck condition. If the inhomogeneus spin linewidth $\delta\omega_0$ exceeds the spin-phonon gap frequency $\Delta/\hbar$, the splitting of spin and phonon modes is not resolved and the oscillations of $p(t)$ are washed out (see Fig. 13).

Inclusion of the *ad hoc* phonon relaxation rate Γ_{ph} in the theory describes the second, postplateau, stage of the spin relaxation. An important observation is that for $B \gg 1$, the corresponding relaxation rate is much smaller than Γ_{ph} (see Figs. 8 and 14) and the spin relaxation is nonexponential [see Eq. (49) and Fig. 9]. One should stress, however, that it is not completely satisfactory to plug an *ad hoc* phonon relaxation into the theory. The latter should be treated in this case as taken from the experiment. This can lead to a problem since one of the main sources of the observed phonon damping can be their scattering on spins that is already taken into account by the very spin phonon interaction [Eq. (4)]. On the other hand, this and other kinds of elastic scattering cannot help the system to reach complete equilibrium since these processes conserve the energy and do not transfer excitation from the narrow group of resonant phonons to the rest of the phonon bath.

It would be of principal importance to generalize the theory of phonon bottleneck for the highly excited initial states of the spin subsystem. However, the Schrödinger equation in this case is not amenable to a direct numerical solution. In Ref. 12 it was argued that, since collective motion of spins in the regions large in comparison to the typical distance between the neighboring spins involves a large number of atomic spins, the problem can be considered classically. Thus, the spin and phonon operators in Eqs. (9) and (10) of Ref. 12 had been replaced by classical variables. This gives a possibility to numerically treat highly excited states of the spin-phonon system without the combinatorial explosion of the full SE. On the other hand, linearization of the classical equations of motion of Ref. 12 near the ground state yields equations that are equivalent to the truncated SE [Eq. (7)] in

the low-excitation limit. This suggests that classical equations of Ref. 12 are indeed a good approximation for the spin-phonon problem in the whole energy range. It would be interesting to investigate what are quantum corrections to these equations.

ACKNOWLEDGMENTS

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