Relaxation of superparamagnetic spins: Classical vs large-spin description

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Effective giant spins of magnetic nanoparticles are considered classically in the conventional theory of superparamagnetism based on the Landau-Lifshitz-Langevin equation. However, microscopic calculations for a large spin with uniaxial anisotropy, coupled to the lattice via the simplest generic mechanism, show that the results of the conventional theory are not reproduced in the limit $S \to \infty$. In particular, the prefactor Γ_0 in the Arrhenius escape rate over the barrier $\Gamma = \Gamma_0 \exp[-\Delta U/(k_B T)]$ has an anomalously large sensitivity to symmetry-breaking interactions such as transverse field.

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I. INTRODUCTION

Ferromagnetic particles of a sufficiently small size (e.g., magnetic nanoparticles) are in a single-domain magnetic state, atomic spins being kept collinear by a strong exchange interaction. The resulting giant spin of a magnetic particle shows a bistability in the case of uniaxial anisotropy that creates two energy minima and a barrier between them.[1,2] At thermal equilibrium, there is a distribution over directions of particles' spins similar to that of paramagnets. Since total spins of magnetic particles are very large, this kind of paramagnetism is called "superparamagnetism."

Néel[3] suggested a model of relaxation of ensembles of magnetic particles in which spins are thermally hopping between the two energy minima. Modern approach to superparamagnetic dynamics is based on the Landau-Lifshitz equation[4] for classical-spin vectors of unit length $|\mathbf{s}|=1$ augmented by the stochastic Langevin field simulating the environment,[5]

$$\dot{\mathbf{s}} = \gamma[\mathbf{s} \times (\mathbf{H}_{\text{eff}} + \boldsymbol{\zeta})] - \gamma\alpha[\mathbf{s} \times (\mathbf{s} \times \mathbf{H}_{\text{eff}})], \tag{1}$$

where γ is the gyromagnetic ratio and $\alpha \ll 1$ is the damping constant. The correlators of the $\alpha, \beta = x, y, z$ components of the Langevin field $\boldsymbol{\zeta}(t)$ are given by

$$\langle \zeta_\alpha(t) \zeta_\beta(t') \rangle = \frac{2\alpha T}{\gamma \mu_0} \delta_{\alpha\beta} \delta(t - t'), \tag{2}$$

where μ_0 is the magnetic moment associated with the spin $\mathbf{s}$. The field $\mathbf{H}_{\text{eff}}$ in Eq. (1) is the effective field defined by $\mathbf{H}_{\text{eff}} = -\mu_0^{-1} \partial \mathcal{H}/\partial \mathbf{s}$, where $\mathcal{H}$ is the classical energy of the spin. The mostly studied generic expression, the whetstone for theoretical approaches, has the form

$$\mathcal{H} = -d s_z^2 - \mu_0 \mathbf{H} \cdot \mathbf{s}, \tag{3}$$

where the uniaxial anisotropy d accounts for the bistability of magnetic particles and $\mathbf{H}$ is the external magnetic field that can have both longitudinal and transverse components. Transverse field creates a saddle in the energy $\mathcal{H}$, whereas in the purely longitudinal case there is no saddle and the barrier corresponds to $\theta = \theta_0$ in the representation of the spin by the angles (θ, φ). Other types of anisotropies such as biaxial and cubic anisotropies can be added to Eq. (3). The stochastic model above is equivalent to the Fokker-Planck equation (FPE). Solution of the FPE yields the Arrhenius thermal activation rate $\Gamma = \Gamma_0 \exp[-\Delta U/(k_B T)]$ for $T \ll \Delta U/k_B$, with ΔU being the energy barrier.[5,6]

The amount of theoretical papers published on the subject up to now is innumerable. The reader can refer to the book[7] on the Langevin approach to magnetic and dipolar systems, and to Ref. 8 for a review of spin thermal activation problems. Numerically one can solve the FPE using matrix-continued fractions[9] or other methods. Alternatively, one can start with the underlying stochastic model and solve it with matrix-continued fractions[10] or directly as a stochastic differential equation,[11,12] also for the model with a variable spin length near the Curie temperature.[13] For a model of many classical atomic spins forming a nanoparticle, direct solution of a system of Landau-Lifshitz-Langevin (LLL) equations is the only working numerical method.[14]

Experimentally, only recent successes in fabrication of nanoparticles with well-controlled parameters allowed the obtaining of the famous Stoner-Wohlfarth astroid and checking of the Néel-Brown theory of thermal activation.[15–17] On smaller nanoparticles, indications of spin tunneling[18–21] have been seen.[22] Later, however, the interest in spin tunneling has shifted to molecular magnets such as Mn_{12} and Fe_8, where the molecular spin is only $S=10$ and the phenomenon could be observed with a much greater certainty and resolution.[23–27]

The stochastic model of magnetic particles using the Landau-Lifshitz equation for a large spin with the formal Langevin magnetic field has been perpetuated in the literature because of its simplicity. However, this model contradicts the time-reversal symmetry. Deformations of the lattice due to thermal fluctuations cannot produce any fluctuating effective magnetic field (i.e., terms in the Hamiltonian *linear* in spin components). It rather produces a fluctuating anisotropy, i.e., stochastic terms *even* in components of the spin $\mathbf{s}$. The corresponding analysis has been done in Ref. 28 where it was shown how the symmetry and strength of the relaxation term in the Landau-Lifshitz equation follows from those of the stochastic terms. However, this model for classical spins was never used because it includes too many difficult-to-define coupling and damping constants.

Another important issue that is the subject of this paper is that microscopic calculations of relaxation rates yield results depending on quantum-mechanical energy levels of the system, whereas in the stochastic model above, the information of the energy levels is completely lost. In the quantum theory the distances between the levels involved, i.e., the transition frequencies ω_{mn}, are of a primary importance since the rates of the usually dominant direct emission or absorption spin-phonon processes are powers of ω_{mn}. Quantum consideration of the relaxation of a magnetic particle (spin) to a phonon bath or any other bath is based on the density-matrix equation (DME) (see, e.g., Ref. 29) written in some basis of states for the quantum spin. As an example one can mention applications of the DME to molecular magnets.[30–35]

The density-matrix equation describes both spin tunneling and thermal activation, and it is a quantum counterpart of the FPE for classical spins mentioned above. Finding a quantum-classical correspondence for large spins $S \gg 1$ is an interesting problem addressed in recent publications.[35–38] For the quantum analog of Eq. (3) with a purely longitudinal field,[36–38] the DME written in the basis of eigenstates $|m\rangle$ of the operator S_z is nothing else than a discrete approximation to the FPE so that finding the quantum-classical correspondence is easy. However, the FPE following from Eq. (1) can be only reproduced if the bath is assumed to have white-noise statistical properties of Eq. (2) that excludes the most important phonon bath. For the model with transverse field or transverse anisotropies, quantum-classical correspondence can be found using quantum distribution functions based on spin coherent states. The formalism can be found in Ref. 38, however, for the purely longitudinal model. Again, a white-noise bath was assumed to connect to Eq. (3) so that there is no dependence on the transition frequencies of the quantum spin.

In the case with transverse field, some DME calculations[30,32,35] have been performed using the $|m\rangle$ basis, whereas others[31,33,34] used the basis of exact spin eigenstates. For the problem of thermal activation over the barrier, the latter is preferable since, in the most important region near the top of the barrier, the exact levels and ensuing transition rates are strongly influenced even by a weak transverse field. Still, Ref. 35 well reproduces the classical limit of the magnetic-resonance line shape resulting from adding many quantum transitions in the limit $S \gg 1$. Such a line shape has been recently observed on magnetic particles in Ref. 39 and theoretically explained with the so-called "quantization approach" that should be valid in the classical limit as well.

Realistic microscopic quantum-mechanical models of spin-lattice relaxation, unlike the idealized white-noise-bath models, employ spin-lattice couplings resulting from changing the crystal field by phonons. Until recently, however, these calculations suffered from too many unknown coupling constants that allowed only order-of-magnitude estimations. Discovery of the universal mechanism of spin relaxation via distortionless rotation of the crystal field by transverse phonons[40,41] changed the situation. Currently it is possible to calculate relaxation rates without approximations and using unknown parameters.

The aim of this paper is to demonstrate that relaxation of large spins, such as spins of magnetic particles, cannot be described by the conventional classical approach using Eq. (1). As mentioned above, the most important quantum-mechanical relaxation processes such as emission or absorption of phonons are sensitive to the energy levels of the spin that are lost in Eq. (1). One can argue that giant spins of magnetic particles, $S \ggg 1$, are classical to a high degree of precision. This is not true, however, since even the relaxation in the bulk is governed by quantum mechanics. Of course, equilibrium properties of superparamagnets are classical since one has the Langevin function instead of the Brillouin function for the field-dependent magnetization. The relaxation remains nonclassical however large is the particle.

To understand the importance of quantum effects in magnetic particles, one has to realize the difference between the *classical-spin limit* and the *large-spin limit*. The classical-spin limit is a theoretical trick to simplify calculations by eliminating quantum effects. An example are models considering classical spin-vectors $|\mathbf{s}|=1$ on each lattice site i, such as models used to describe many-body dynamics of magnetic particles taking into account internal noncollinearities of individual spins (see, e.g., Refs. 42–46). Solution of dynamical problems of this kind on the quantum-mechanical level currently seems to be unfeasible. It should be noted that the transition frequencies for the classical-spin models are formally zero so that there are no direct phonon processes.

Magnetic particles with the exchange interaction being so strong that all N individual spins S_0 are bound into a single effective spin $S=NS_0 \gg 1$ represent the large-spin limit. The resulting large spin can be considered quantum mechanically, which reveals that it is not a fully classical spin. Indeed, the energy barrier is $\Delta U = DS^2 = ND_0 S_0^2$, proportional to the size of the particle, as it should be. With $S=NS_0$ this results in $D=D_0/N$, a fraction of the anisotropy D_0 of an individual spin. Now the transition frequency $\omega_{S,S-1}$ near the bottom of the well is given by $\hbar\omega_{S,S-1}=(2S-1)D \cong 2SD = 2S_0 D_0$, independently of the particle's size. This is not a surprise since $\omega_{S,S-1}$ is the frequency of small-amplitude spin precession in the anisotropy field that is size independent. One can see that direct spin-phonon processes, at least near the bottom of the wells, survive in the large-spin limit $S \gg 1$. This makes the situation completely different from the classical-spin limit, regarding the relaxation.

On the other hand, the transition frequencies between the levels near the top of the barrier, $m \sim 1$, are of order $\hbar\omega_{m,m-1}=(2m-1)D \sim D \propto 1/N$ and they vanish in the large-spin limit. This means that direct phonon processes between the adjacent energy levels, having the rate $\Gamma^{(1)}_{m.m-1} \propto \omega^2_{m,m-1}$ for $\hbar\omega_{m,m-1} \ll k_B T$, die out near the top of the barrier that becomes a bottleneck for the thermal activation process. In this region, diffusion of spin populations over the stairway of adjacent levels is effectuated by much weaker Raman processes that lead to small escape prefactors Γ_0 with essential temperature dependence.[47]

Transverse magnetic field $H_\perp$ or transverse anisotropy creates saddles in the potential landscape of the effective spin that strongly change dynamics of thermal activation. A "phase diagram" of different regimes, such as uniaxial, high-damping (HD), intermediate-damping, and low-damping (LD) regimes, created by the transverse field, has been obtained in Ref. 48. Especially in the LD case, transverse field results in a strong increase in the escape rate Γ. As can be seen from the comparison of the LD and HD cases in Fig. 3 of Ref. 48, the main effect is the increase in the prefactor Γ_0

while lowering the barrier ΔU (equal in the LD and HD cases) plays a secondary role.

For a quantum large spin, the effect of transverse field $H_\perp$ should be even greater since for $H_\perp=0$ the prefactor Γ_0 is anomalously small. For $H_\perp \neq 0$, the states $|m\rangle$ are no longer eigenvalues of the spin Hamiltonian $\mathcal{H}$ and spin hopping is no longer restricted to adjacent levels. Thus transverse field should resolve the bottleneck near the top of the barrier, leading to a huge increase in the escape prefactor Γ_0. The aim of the present work is to describe this effect by solving the DME that is a quantum counterpart of the FPE. The universal mechanism of spin-lattice relaxation[40,41] has been recently incorporated into the DME.[34] Here it will be used to obtain the results with only one parameter describing the spin-phonon interaction, the characteristic energy $E_t \equiv (\rho v_t^5 \hbar^3)^{1/4}$, where ρ is the mass density of the lattice and v_t is the speed of transverse sound. The model used here is on the same level of simplicity as the standard Landau-Lifshitz-Langevin equation or the FPE but it is much better justified. We will see that quantum effects on the thermal activation rate Γ do not vanish and become even stronger in the large-spin limit $S \ggg 1$ for nearly uniaxial magnetic particles that invalidates Eq. (1).

II. THERMALLY ACTIVATED ESCAPE RATE OF A LARGE QUANTUM SPIN

The effective-spin Hamiltonian has the form

$$\hat{H}_S = \hat{H}_A + \hat{H}_Z, \tag{4}$$

where $\hat{H}_A$ is the crystal-field (anisotropy) Hamiltonian and $\hat{H}_Z$ is the Zeeman Hamiltonian,

$$\hat{H}_A = -DS_z^2, \quad \hat{H}_Z = g m_B (H_z S_z + H_x S_x). \tag{5}$$

The classical energy barrier ΔU has particular forms

$$\Delta U = DS^2 \begin{cases} (1-h_x)^2, & h_z = 0 \\ (1-h_z)^2, & h_x = 0 \end{cases}, \tag{6}$$

where $h_{x,z} \equiv g m_B H_{x,z}/(2SD)$. In general $\Delta U(h_x,h_z)$ can be visualized as a Stoner-Wohlfarth astropyramid, completely symmetric in h_x and h_z, and basing on the astroid $h_x^{2/3}+h_z^{2/3}=1$.

In the absence of the transverse field H_x, the eigenstates of the spin are $|m\rangle$, $m=-S,\ldots,S$, the energy levels being

$$\varepsilon_m = -Dm^2 - g m_B H_z m. \tag{7}$$

Condition $\hbar\omega_{mm'} \equiv \varepsilon_m - \varepsilon_{m'} = 0$ for $m \neq m'$ defines the resonance values of the longitudinal field H_z:

$$g m_B H_z = kD, \quad k = 0, \pm 1, \pm 2, \ldots. \tag{8}$$

For these fields *all* levels in the right well $m'=-m-k$ are at resonance with the corresponding levels in the left well, $m<0$.

The magnetic particle can be considered as embedded in the elastic matrix described by the harmonic-phonon Hamiltonian $\hat{H}_{\rm ph} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda}^\dagger a_{\mathbf{k}\lambda}$. Approach developed in Refs. 40 and 41 allows avoidance of using unknown spin-phonon coupling constants and a great simplification of the formalism. Since this formalism is well documented in the literature (see, in particular, Ref. 34), its presentation here will be brief. Considering the lattice locally rotated by transverse phonons without distortion of its crystal field, one obtains the spin-phonon interaction

$$\hat{H}_{\rm s-ph} = \hat{R}\hat{H}_A\hat{R}^{-1} - \hat{H}_A, \quad \hat{R} = e^{-i\mathbf{S}\cdot\delta\boldsymbol{\phi}}, \tag{9}$$

where $\delta\boldsymbol{\phi}$ is a small rotation angle given by $\delta\boldsymbol{\phi}=(1/2)\nabla \times \mathbf{u}(\mathbf{r})$, $\mathbf{u}(\mathbf{r})$ being the lattice displacement due to phonons. Expanding Eq. (9) up to first order in $\delta\boldsymbol{\phi}$ yields the spin-phonon interaction that describes one-phonon processes:

$$\hat{H}_{\rm s-ph}^{(1)} = i[\hat{H}_A, \mathbf{S}] \cdot \delta\boldsymbol{\phi}. \tag{10}$$

It is important that the spin-phonon interaction above does not include any poorly known spin-lattice coupling coefficients and it is entirely represented by the crystal field $\hat{H}_A$. To describe the two-phonon (Raman) processes, one has to expand $\hat{H}_{\rm s-ph}$ up to the second order in $\delta\boldsymbol{\phi}$.[34,49] Relaxation rates due to Raman processes are generally much smaller than those due to the direct processes since they are the next order in the spin-phonon interaction. However, the rates of direct processes can be small for special reasons, then Raman processes become important. Here it happens indeed near the top of the barrier in zero transverse field, where the transition frequencies between adjacent levels become small. This situation has been studied in detail in Ref. 47, however. So we will neglect Raman processes here and concentrate on the effect of the transverse field that changes transition frequencies and drastically increases the escape rate.

We use the canonical quantization of the lattice displacement $\mathbf{u}$ that yields

$$\delta\boldsymbol{\phi} = \frac{1}{2}\sqrt{\frac{\hbar}{2MN}} \sum_{\mathbf{k}\lambda} \frac{[i\mathbf{k}\times\mathbf{e}_{\mathbf{k}\lambda}] e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\omega_{\mathbf{k}\lambda}}} (a_{\mathbf{k}\lambda} + a_{-\mathbf{k}\lambda}^\dagger). \tag{11}$$

Here M is the mass of the unit cell, N is the number of cells in the crystal, $\mathbf{e}_{\mathbf{k}\lambda}$ are unit polarization vectors, $\lambda = t_1, t_2, l$ denotes polarization, and $\omega_{k\lambda} = v_\lambda k$ is the phonon frequency. Only transverse phonons, $\mathbf{e}_{\mathbf{k}\lambda} \perp \mathbf{k}$, survive in this formula.

Spin-lattice relaxation including thermal activation can be described by the DME.[29,34] Early application of the DME to the present model in Ref. 30 used the natural basis of states $|m\rangle$. This provided an overall satisfactory description of the thermal activation rate, including its strong increase at resonance values of H_z given by Eq. (8). On the other hand, exact energy levels $|\alpha\rangle$ of the spin strongly differ from $|m\rangle$ near the top of the barrier even for a small H_x. For this reason, the DME below will be written with respect to the energy basis $|\alpha\rangle$ obtained by numerical diagonalization of $\hat{H}_S$.[34]

The relaxation terms in the DME can be represented in the form that does not explicitly contain $\hat{H}_A$: the information about it being absorbed in the spin eigenstates $|\alpha\rangle$ and transition frequencies $\omega_{\alpha\beta}$. This can be achieved either by changing from the laboratory frame to the local lattice frame in which $\hat{H}_A$ remains constant but an effective rotationgenerated magnetic field arises,[21,40,41] or by manipulating matrix elements of the spin-phonon interaction with respect to exact spin states, $\langle\alpha|\hat{H}^{(1)}_{\text{s-ph}}|\beta\rangle$.[41] Both methods are mathematically equivalent.[41] As a result, the spin part of spin-phonon matrix elements is given by the universal expression

$$\Xi^{(1)}_{\alpha\beta} \equiv i\langle\alpha|[\hat{H}_A,\mathbf{S}]|\beta\rangle = i\hbar\omega_{\alpha\beta}\langle\alpha|\mathbf{S}|\beta\rangle - \langle\alpha|\mathbf{S}|\beta\rangle \times g\mu_B\mathbf{H}. \tag{12}$$

At tunneling resonances [Eq. (8)], one has to use the full nonsecular form of the DME that couples diagonal elements of the density matrix, $\rho_{\alpha\alpha}=n_\alpha$, to nondiagonal elements.[34] In the sequel, tunneling resonances will be avoided by choosing the bias field H_z in the middle between the resonances to make a better connection with classical models. In this case, one can use the system of rate equations for the level populations,

$$\frac{d}{dt}n_\alpha = \sum_{\alpha'=1}^{2S+1}(\Gamma_{\alpha\alpha'}n_{\alpha'} - \Gamma_{\alpha'\alpha}n_\alpha), \tag{13}$$

where relaxation rates are given by

$$\Gamma_{\alpha\alpha'} = 2(|\Xi^{(1)}_{\alpha\alpha'}|/D)^2[\Gamma^{(1)}(\omega_{\alpha'\alpha})(n_{\omega_{\alpha'\alpha}}+1) + \Gamma^{(1)}(\omega_{\alpha\alpha'})n_{\omega_{\alpha\alpha'}}]. \tag{14}$$

Here $n_\omega \equiv (e^{\hbar\omega/(k_BT)}-1)^{-1}$ and

$$\Gamma^{(1)}(\omega) \equiv \frac{|\omega|^3 D^2}{24\pi\hbar^2\Omega_t^4}\theta(\omega), \tag{15}$$

$\theta(\omega)$ being a Heaviside function and $\Omega_t \equiv (\rho v_t^5/\hbar)^{1/4}$ being a characteristic frequency. In Eq. (13) transitions occur between all the exact spin levels α although $\Gamma_{\alpha\alpha'}$ corresponding to pairs of adjacent levels are still dominating. On the other hand, small transition rates $\Gamma_{\alpha\alpha'}$ near the top of the barrier are strongly modified even for $h_x \ll 1$. The coupling of the spin to the environment is gauged by a single parameter, Ω_t in Eq. (15), similarly to the parametrization by the dimensionless damping constant α in the classical LLL equation. However, in the present quantum model the rate $\Gamma^{(1)}(\omega)$ is frequency dependent through the distances between energy levels that have no analog in the classical scheme.

Numerical solution of Eq. (13) for the parameters of the molecular magnet Mn_{12} ($S=10$, $D/k_B=0.65$ K) shifted away from the zero-field resonance, $gm_BH_z=0.5D$, shows a huge dependence on the transverse field h_x mainly due to the increase in the prefactor Γ_0 (see Fig. 1). The contribution of the Arrhenius exponent $\exp[-\Delta U/(k_BT)]$ to the growth of $\Gamma(h_x)$, shown by straight lines $\exp[2h_xDS^2/(k_BT)]$ following from Eq. (6), becomes important only on the right side of the plot where the growth of $\Gamma_0(h_x)$ saturates. The effect of the transverse field here is much greater than in the classical model, the LD curve in Fig. 3 of Ref. 48. Note that in the present model we are in the uniaxial-low-damping limit since the damping calculated here from the first principles for realistic Ω_t is much smaller than all other frequency scales.

For effective spins of magnetic particles that are much greater than $S=10$, the effect of the transverse field is huge.

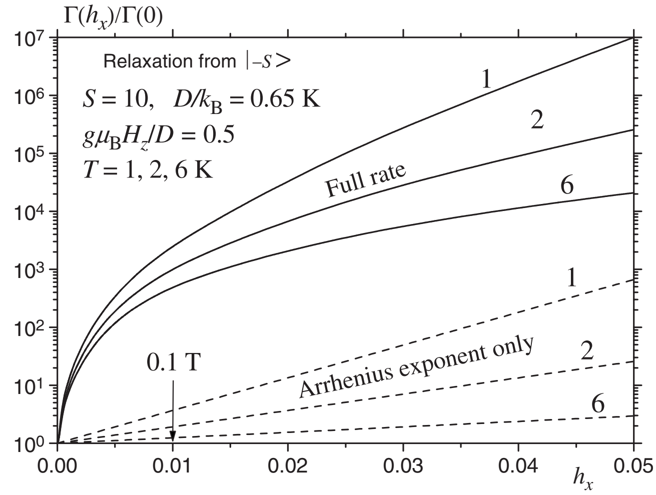

FIG. 1. Reduced thermal activation rate vs transverse field for different temperatures and $S=10$, $D/k_B=0.65$ K. Dramatic increase in Γ at small h_x is due to that of the prefactor Γ_0, whereas the activation exponent (straight dashed lines) gives a comparatively moderate growth.

Since Γ in zero transverse field becomes anomalously small for large spins, one cannot normalize the results by it. It is better to plot the prefactor Γ_0 alone, defined as $\Gamma_0 = \Gamma\exp[\Delta U/(k_BT)]$, where Γ follows from the solution of Eq. (13) and ΔU is found numerically for the classical model. The characteristic rate,

$$\tilde{\Gamma} \equiv S\Gamma_{S,S-1} = \frac{S^2\omega^5_{S,S-1}}{12\pi\Omega_t^4}, \tag{16}$$

can be used to normalize the results for Γ_0 in a wide range of h_x. Here $\Gamma_{S,S-1}$ and $\omega_{S,S-1}$ are zero-temperature relaxation rate and transition frequency for the lowest-lying pair of levels in the well, defined above. $\tilde{\Gamma}=S\Gamma_{S,S-1}$ is an overall measure of the relaxation rate inside a well. Indeed, in the natural basis the spin-phonon transition rate between two adjacent levels is proportional to $\bar{l}^2_{m,m\pm1}$,[30] where $\bar{l}_{m,m\pm1} \equiv l_{m,m\pm1}(2m\pm1)$ and $l_{m,m\pm1}=\sqrt{S(S+1)-m(m\pm1)}$. In $\Gamma_{S,S-1}$ the factor $\bar{l}^2_{m,m\pm1}$ yields S while for a typical value of m in the interval $-S\le m\le S$ it yields S^2. This is the origin of an additional S in Eq. (16).

In the comparison between different values of S shown in Fig. 2, the product SD is kept constant, as it should be for the effective anisotropy of magnetic particles. In numerical calculations $D/k_B=6.5/S$ K is used and the temperature $k_BT = SD=$const. Figure 2(a) shows that curves $\Gamma_0/\tilde{\Gamma}$ scale for large S in a wide range of h_x, which means $\Gamma_0 \propto S^2$. Calculations use custom-precision matrix algebra within Wolfram Mathematica and become slow for spins as large as $S=80$. One can see that in the large-spin limit Γ_0 becomes small if $h_x\to0$ and $h_x\to1$. In particular, for $h_x\to0$ the apparent behavior is $\Gamma_0\propto h_x^2$.

The behavior of Γ_0 at small transverse fields is elucidated in Fig. 2(b). Here one has to use a slightly different normalization of Γ_0 to make curves collapse in a wide range of h_x, yielding $\Gamma_0\propto S^{3/2}h_x^2$. In the uniaxial limit $h_x\to0$ the curves

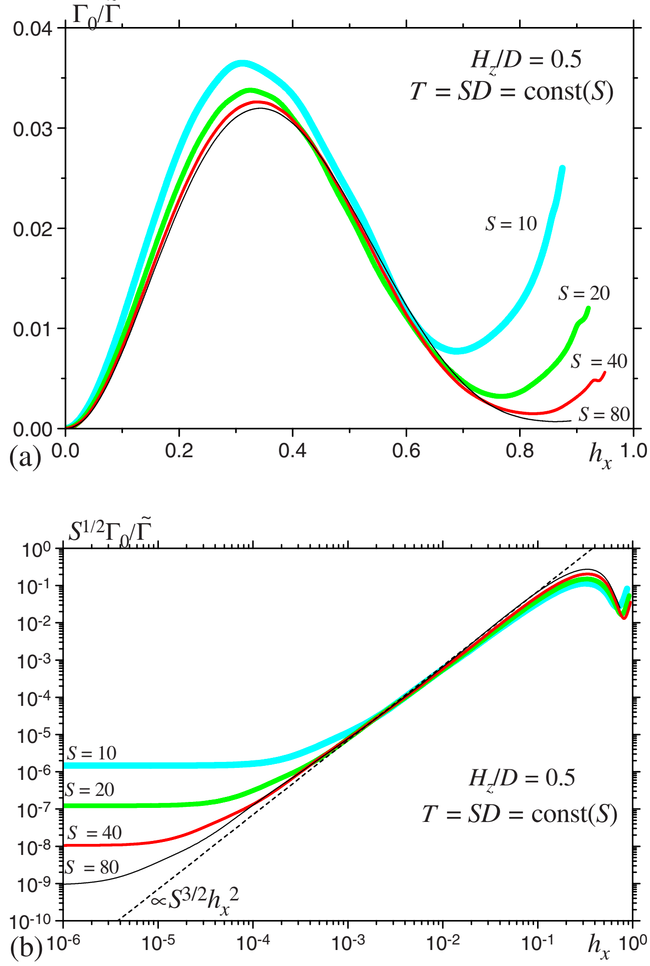

FIG. 2. (Color online) Escape-rate prefactor Γ_0 vs transverse field for different values of particle's spin S at fixed temperature.

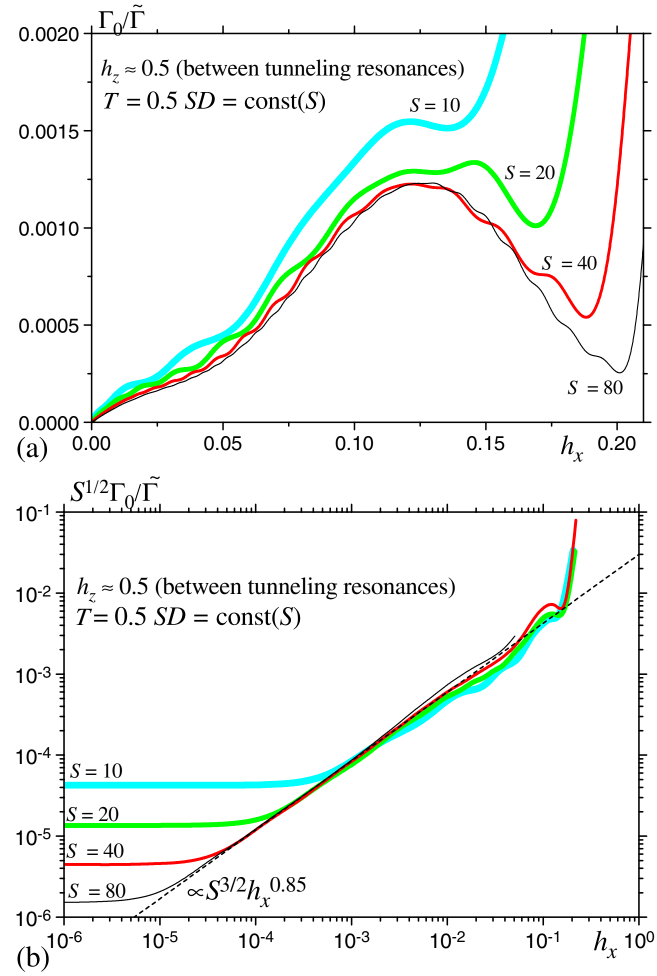

FIG. 3. (Color online) Escape-rate prefactor Γ_0 vs transverse field for different values of particle's spin S at fixed temperature at strong bias, $h_x \approx 0.5$ (between tunneling resonances).

for different S diverge. Here the escape prefactor is given by the transition rate between the adjacent levels near the top of the barrier $\Gamma_{m,m\pm1}$ with $m \simeq 1$. Using Eq. (A9) of Ref. 41 for $\Gamma_{m,m\pm1}$ [multiplied by $n_{\omega_{m,m\pm1}} \cong k_B T/(\hbar\omega_{m,m\pm1})$ to account for a nonzero temperature], one obtains $\Gamma_0 \propto S^{-2}$. This is the top-of-the-barrier bottleneck mentioned in Sec. I. In the representation of Fig. 2(b) one has $\Gamma_0/S^{3/2} \propto S^{-7/2}$. One can see that doubling S results in the drop by a factor of $2^{7/2} \simeq 11$ in the asymptotic $h_x \to 0$ values in Fig. 2(b).

The anomalously small rate in the uniaxial limit above is in part due to the factor $2m \pm 1$ discussed below Eq. (16). In the zero-bias case the top of the barrier corresponds to $m \sim 1$, which results in additional smallness. In the case of a strong enough bias, one has $2m \pm 1 \sim S$ near the top of the barrier so that the anomalously small escape rate solely results from small $\omega_{m,m\pm1}$. The results of numerical calculations for the bias $h_x \approx 0.5$, adjusted to the middle between two tunneling resonances are shown in Fig. 3. The curves for Γ_0 in a broad range of h_x in Fig. 3(a) look complicated for moderate S but still collapse for large S. The decrease in Γ_0 at $h_x \to 0$ is indeed weaker than in the unbiased case above. The results at small h_x in Fig. 3(b) show a dependence $\Gamma_0 \propto S^{3/2} h_x^{0.85}$, where the exponent 0.85 cannot be easily explained. For $h_x = 0$ Eq. (A9) of Ref. 41 yields $\Gamma_0 \propto S^0$ in the biased case, also much smaller than $\Gamma_0 \propto S^2$ for $h_x \sim 1$.

It should be noted that the secular approximation leading to Eq. (13) relies on the smallness of the relaxation terms in the DME in comparison to the dissipationless terms for the nondiagonal elements of the density matrix.[34] Then slow diagonal elements $\rho_{\alpha\alpha} = n_\alpha$ dynamically decouple from the fast nondiagonal terms $\rho_{\alpha\beta}$. The classical match of the secular approximation is the LD approximation introduced by Kramers[50] for a particle in a potential well. In the LD limit the energy of the particle or spin is nearly conserved so that the fast motion over constant-energy trajectories averages out and what is left is the slow energy diffusion (see, e.g., Eqs. (15) and (16) of Ref. 48). Similarly, Eq. (13) describes a slow hopping over the quantum energy levels of the spin.

One can ask whether the richness of damping regimes that exist in the classical-spin model[48] can be realized for a realistic large quantum spin of a magnetic particle. For instance, the intermediate-to-high damping (IHD) case requires that the gyroscopic and relaxation terms in the FPE be comparable. This means that the dissipationless and relaxation terms in the DME be comparable as well. Of course, for $S \gg 1$ nondiagonal elements $\rho_{\alpha\beta}$ close to diagonal become slow as $\omega_{\alpha\beta}$. However, the relaxation rate $\Gamma_{\alpha\beta}$ between the states α and β scales as $\Gamma_{\alpha\beta} \propto \omega_{\alpha\beta}^2$ for $|\omega_{\alpha\beta}| \ll T$, and decreases faster than $\omega_{\alpha\beta}$ in the quasiclassical limit $S \gg 1$.

What can change the situation is Raman processes that become independent of $\omega_{\alpha\beta}$ for small $\omega_{\alpha\beta}$. Incorporating Raman processes requires generalization of the results of Ref. 47 for a nonzero transverse field that is a nontrivial task. As Raman processes are much weaker than direct processes, crossover to a Raman-dominated behavior requires very large S. Although a general nonsecular DME can be solved as described in Ref. 34, calculations are much slower than those of Eq. (13) and become prohibitive for the required very large S. For this reason, Raman processes cannot be adequately treated within this paper and should be considered elsewhere.

In all cases, even with account of Raman processes, there should be a bottleneck for spin diffusion near the top of the barrier in the case of nearly uniaxial magnetic particles. Transverse magnetic field gradually resolves the bottleneck and leads to a huge increase in the escape-rate prefactor Γ_0 that is more important than the barrier lowering.

III. CONCLUSION

Huge dependence of the thermal activation prefactor Γ_0 due to spin-phonon processes on the transverse field for a large quantum spin $S \gg 1$ is the main finding of this work. Although a high sensitivity to the transverse field in the low-damping regime has been also found[48] for classical spins described by Eq. (1), the present quantum dependence is much stronger. This is due to the peculiar dependence of the relaxation rate on the distances between the energy levels of the spin that is lost in Eq. (1). The example shows that particles with large effective spins do not behave classically in their relaxation.

The striking result of the paper is, actually, not totally surprising since all papers studying the quantum-classical correspondence in the spin relaxation, such as Refs. 35–38, used a simplified model of the bath with white-noise correlation. From the derivations in these papers, one can see that for other models of the bath, such as the phonon bath, Eq. (1) does not result in the limit $S \gg 1$. The present paper simply demonstrates this fact explicitly for a clean particular model [Eq. (3) or (5)] that was studied in a great number of publications.

It was found that thermal activation rates of nearly uniaxial magnetic particles are very sensitive to any deviation from the axial magnetic symmetry, e.g., due to dipolar fields, surface anisotropy, and different kinds of transverse crystallographic anisotropy. This means that in practical cases the extremely strong dependence of the prefactor Γ_0 on the small transverse field will be killed by the "dirt" so that Γ_0 becomes difficult to define theoretically. Of course, this fact does not prove that the phenomenological classical Eq. (1) becomes valid.

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