Are superparamagnetic spins classical?

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Abstract. - 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 \( \Gamma_0 \) in the Arrhenius escape rate over the barrier \( \Gamma = \Gamma_0 \exp \left[ -\Delta U / (k_B T) \right] \) has an anomalously large sensitivity to symmetry-breaking interactions such as transverse field.

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 suggested a model of relaxation of ensembles of magnetic particles in which spins are hopping between the two energy minima [3]. Modern approach to superparamagnetic dynamics is based on the Landau-Lifshitz equation [4] for classical spins of fixed length augmented by the stochastic Langevin field simulating the environment [5] that is equivalent to the Fokker-Planck equation (FPE) for classical spins. Solution of the FPE yields the Arrhenius thermal activation rate \( \Gamma = \Gamma_0 \exp \left[ -\Delta U / (k_B T) \right] \) for \( T \ll \Delta U / k_B \), \( \Delta U \) 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].

With increasing the size of a magnetic particle, noncollinearities due to the surface anisotropy proliferate and the single-domain state is gradually destroyed. Small noncollinearities result in an additional cubic anisotropy for particle’s global magnetization [15–17] that is second-order in the surface-anisotropy constant and scales as the particle’s volume. Another interesting effect is relaxation via internal spin waves [18, 19] that should add up with the relaxation due to the environment.

Experimentally, only recent successes in fabrication of nanoparticles with well-controlled parameters allowed to obtain the famous Stoner-Wohlfarth astroid and check the Néel-Brown theory of thermal activation [20–22]. On smaller nanoparticles, indications of spin tunneling [23–26] have been seen [27]. 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 [28–32].

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 S. The corresponding analysis has been done in Ref. [33] 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 can include too many difficult-to-define coupling and damping constants.

On the other hand, all microscopic quantum-mechanical models of spin-lattice relaxation employ spin-lattice couplings that do not violate basic symmetries. 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 [34,35] changed the situation. Within this mechanism, spin-lattice coupling can be expressed through the parameters of the crystal field that can be easily measured. Implementing this mechanism in the stochastic formalism for classical spins of Ref. [33] would allow to rewrite the theory of superparamagnetism in a more satisfactory form.

The less ambitious aim of this Letter is, however, just to demonstrate that relaxation of large spins of magnetic particles cannot be described by the conventional classical approach. The point is that the most important quantum-mechanical relaxation processes such as emission/absorption of phonons are sensitive to the energy levels of the spin. Since in the existing LLL formalism the information of the energy levels is lost, there is no connection to the underlying quantum mechanics and the ensuing results are questionable.

One can argue that giant spins of magnetic particles, \( S \gg 1 \), 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 non-classical, however, whatever large is the particle. Indeed, quantum effects in magnetic particles have been recently observed and discussed in Ref. [36].

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. The large-spin limit, to the contrary, is the real situation.

For instance, for a system of \( N \) atomic spins \( s \) with the easy-axis Hamiltonian \( \hat{H} = -ds^2 \), held together by a strong exchange, the total spin is \( S = Ns \gg 1 \). Within the classical-spin limit, the effective classical Hamiltonian of the system would be \( \hat{H} = -Ds^2 \) with \( D = d/N^2 \) to preserve the energy barrier \( \Delta U = ds^2 = DS^2 \). With the energy levels of the spin \( S \) given by \( \varepsilon_m = -Dm^2 \), the transition frequency \( \omega_{S-1,S} = \varepsilon_{S-1} - \varepsilon_S \) between the ground and first excited states of the effective spin becomes \( \hbar \omega_{S,S-1} = (2S - 1)D \equiv 2sd/N \), disappearing in the limit \( N \to \infty \). Accordingly, the direct phonon processes die out for large \( N \), so that the only relaxation processes due to phonons become the two-phonon Raman processes that become insensitive to the energy levels for small transition frequencies.

In the realistic large-spin limit, the transition frequency \( \omega_{S,S-1} \) is preserved, because this is the frequency of the small-amplitude spin precession in the anisotropy field. Thus the effective anisotropy constant \( D \) scales according to \( \hbar \omega_{S,S-1} = (2S - 1)D \equiv 2sd/N \). In this case the energy barrier is \( \Delta U = DS^2 = Nd^2 \alpha N \), the size of the particle, as it should be. One can see that direct spin-phonon processes survive in the large-spin limit. 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 \( \hbar \omega_{m,m-1} = (2m - 1)D \sim D \alpha 1/N \) and they vanish in the large-spin limit. This means that direct phonon processes between the adjacent even levels, having the rate \( \Gamma_{m,m-1} = \alpha \omega_{m,m-1}^2 \) for \( \hbar \omega_{m,m-1} \ll \kappa B T \), 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 facilitated by much weaker Raman processes that leads to small escape prefactors \( \Gamma_0 \) with essential temperature dependence [37].

Transverse magnetic field \( H_\perp \) or transverse anisotropy create 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-, intermediate-, and low-damping regimes, created by the transverse field, has been obtained in Ref. [38]. Especially in the low-damping (LD) case, transverse field results in a strong increase of the escape rate \( \Gamma \). As can be seen from the comparison of the LD and HD cases in Fig. 3 of Ref. [38], the main effect is the increase of the prefactor \( \Gamma_0 \), while lowering the barrier \( \Delta U \) (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 \( \Gamma_0 \) is anomalously small. For \( H_\perp \neq 0 \), the states \( |m\rangle \) are no longer eigenvalues of the spin Hamiltonian \( \hat{H} \), 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 of the escape prefactor \( \Gamma_0 \). The aim of the present work is to describe this effect by solving the density matrix equation (DME) that is a quantum counterpart of the FPE. The universal mechanism of spin-lattice relaxation [34,35] has been recently incorporated into the DME [39]. Here it
It is important that the spin-phonon interaction above phonon interaction that describes one-phonon processes: all these fields $F_{\alpha \beta}$ for these fields $F_{ph}\equiv \sum_{k\lambda} h_{\omega_{k\lambda}} a^\dagger_{k\lambda} a_{k\lambda}$. Approach developed in Refs. [34,35] allows to avoid using unknown spin-phonon coupling constants and to greatly simplify the formalism. Considering the lattice locally rotated by transverse phonons without distortion of its crystal field, one obtains the spin-phonon interaction

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

where $\delta \phi$ is a small rotation angle given by $\delta \phi = (1/2)\nabla \times \mathbf{u}(\mathbf{r})$, $\mathbf{u}(\mathbf{r})$ being the lattice displacement due to phonons. Expanding Eq. (6) up to first order in $\delta \phi$ yields the spin-phonon interaction that describes one-phonon processes:

$$\hat{H}^{(1)}_{s-ph} = i \left[ \hat{H}_A, \mathbf{S} \right] \cdot \delta \phi. \quad (7)$$

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 $\hat{H}_{s-ph}$ up to the second order in $\delta \phi$ [39,40]. 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. [37], however. So we will neglect Raman processes here and concentrate on the effect of the transverse field that change transition frequencies and drastically increase the escape rate.

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

$$\delta \phi = \frac{1}{2} \sqrt{\frac{\hbar}{2MN}} \sum_{k\lambda} \frac{\left| k \right| \times \mathbf{e}_{k\lambda}}{\sqrt{\omega_{k\lambda}}} \left( a_{k\lambda} + a^\dagger_{-k\lambda} \right). \quad (8)$$

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

Spin-lattice relaxation including thermal activation can be described by the density-matrix equation (DME) [39,41]. Early application of the DME to the present model in Ref. [42] used the natural basis of states $\left| m \right>$. This provided an overall satisfactory description of the thermal activation rate, including its strong increase at resonance values of $H_z$ given by Eq. (5). On the other hand, exact energy levels $\left| \alpha \right>$ of the spin strongly differ from $\left| m \right>$ near the top of the barrier even for a small $H_z$. For this reason, the DME below will be written with respect to the energy basis $\left| \alpha \right>$ obtained by numerical diagonalization of $\hat{H}_S$ [39].

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 $\left| \alpha \right>$ 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 rotation-generated magnetic field arises [26,34,35], or by manipulating matrix elements of the spin-phonon interaction with respect to exact spin states, $\langle \alpha | \hat{H}^{(1)}_{s-ph} | \beta \rangle$ [35]. Both methods are mathematically equivalent [35]. As a result, the spin part of spin-phonon matrix elements is given by the universal expression

$$\Xi^{(1)}_{\alpha\beta} = i \left[ \langle \alpha | \hat{H}_A, \mathbf{S} | \beta \rangle \right] = i\hbar \omega_{\alpha\beta} \langle \alpha | \mathbf{S} | \beta \rangle - \langle \alpha | \mathbf{S} | \beta \rangle \times g\mu_B \mathbf{H}. \quad (9)$$

At tunneling resonances, Eq. (5), one has to use the full non-secular form of the DME that couples diagonal elements of the density matrix, $\rho_{\alpha\alpha} = n_\alpha$, to nondiagonal
elements [39]. 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

$$\frac{d}{dt}n_{\alpha} = \sum_{\alpha' = 1}^{2S+1} (\Gamma_{\alpha\alpha'} n_{\alpha'} - \Gamma_{\alpha'\alpha} n_{\alpha}),$$  \hspace{1cm} (10)$$

where relaxation rates are given by

$$\Gamma_{\alpha\alpha'} = 2 \left( |\Xi^{(1)}|/D \right)^2 [\Gamma^{(1)}(\omega_{\alpha'}) (n_{\omega_{\alpha'}} + 1)] + \Gamma^{(1)}(\omega_{\alpha\alpha'}) n_{\omega_{\alpha'}}. $$  \hspace{1cm} (11)$$

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

$$\Gamma^{(1)}(\omega) \equiv |\omega|^3 D^2 / 24 \pi \hbar^2 \Omega_t^2 \theta(\omega),$$  \hspace{1cm} (12)$$

$\theta(\omega)$ being a Heavyside function and $\Omega_t \equiv (\rho \nu^2 / \hbar)^{1/4}$ being a characteristic frequency. In Eq. (10) transitions occur between all the exact spin levels $\alpha$, 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, $\Omega_t$ in Eq. (12), similarly to the parametrization by the dimensionless damping constant $\alpha$ 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 has no analog in the classical scheme.

Numerical solution of Eq. (10) for the parameters of the molecular magnet $\text{Mn}_{12}$ ($S = 10, D/k_B = 0.65$ K) shifted away from the zero-field resonance, $g m_B H_z = 0.5 D$, shows a huge dependence on the transverse field $h_x$, mainly due to the increase of the prefactor $\Gamma_0$ (see Fig. 1). The contribution of the Arrhenius exponent $\exp[-\Delta U/(k_B T)]$ to the growth of $\Gamma(h_x)$, shown by straight lines $\exp[2h_x DS^2/ (k_B T)]$ following from Eq. (3), 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. [38]. 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 $\Omega_t$ 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. Since $\Gamma$ in zero transverse field becomes anomalously small for large spins, one cannot normalize the results by it. It is better to plot the prefactor $\Gamma_0$ alone defined as $\Gamma_0 = \Gamma \exp[\Delta U/(k_B T)]$, where $\Gamma$ follows from the solution of Eq. (10) and $\Delta U$ is found numerically for the classical model. The characteristic rate

$$\tilde{\Gamma} \equiv S \Gamma_{S,S-1} = \frac{S^2 \omega_{S,S-1}^2}{12 \pi \Omega_t^2}.$$  \hspace{1cm} (13)$$

can be used to normalize the results for $\Gamma_0$ 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. $\tilde{\Gamma} =$
The decrease of $\Gamma_0$ yields $\Gamma_0 \propto S^2$. 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 $\Gamma_0$ becomes small if $h_x \to 0$ and $h_x \to 1$. In particular, for $h_x \to 0$ the apparent behavior is $\Gamma_0 \propto h_x^2$.

The behavior of $\Gamma_0$ at small transverse fields is elucidated in Fig. 2 (b). Here one has to use a slightly different normalization of $\Gamma_0$ 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 $h_x \to 0$ the curves for different $S$ diverge. Here the escape prefactor is given by the transition rate between the adjacent levels near the top of the barrier $\Gamma_{m,m+\pm 1}$ with $m \approx 1$. Using Eq. (10) of Ref. [35] for $\Gamma_{m,m+\pm 1}$ multiplied by $n_{w,m+\pm 1} \equiv k_B T / (\hbar n_{w,m+\pm 1})$ to account for a nonzero temperature, one obtains $\Gamma_0 \propto S^{-2}$. This is the top-of-the-barrier bottleneck mentioned in the introduction. 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 $2^{7/2} \approx 11$ 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. (13). In the zero-bias case the top of the barrier corresponds to $m \sim 1$ that 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 $\omega_{m,m+\pm 1}$. 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 $\Gamma_0$ in a broad range of $h_x$ in Fig. 3 (a) look complicated for moderate $S$ but still collapse for large $S$. The decrease of $\Gamma_0$ 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. [35] 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. (10) 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 [39]. 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 low-damping (LD) approximation introduced by Kramers for a particle in a potential well [43]. 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. [38]). Similarly, Eq. (10) describe 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 [38] can be realized for a realistic large quantum spin of a magnetic particle. For instance, the intermediate-to-large damping (IHD) case requires that the gyroscopic and relaxation terms in the FPE be comparable. This means that the dissipation-less 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 small as $\omega_{\alpha \beta}$. However, the relaxation rate $\Gamma_{\alpha \beta}$ between the states $\alpha$ and $\beta$ 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 quasi-classical 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. [37] 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. [39], calculations are much slower than those of Eq. (10) and become prohibitive for the required very large S. For this reason, Raman processes cannot be adequately treated within this Letter 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 of the escape-rate prefactor $\Gamma_0$ that is more important than the barrier lowering. This is the main finding of this work. Thermal activation rates of nearly-uniaxial magnetic particles are very sensitive to any deviations from the axial magnetic symmetry, e.g., due to surface anisotropy [15–17]. Robust results require a strong enough transverse field.

Whether for large spins the classical stochastic approach could be modified to embrace the spacing between quantum-mechanical levels that has been shown to be important, remains an open question.

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