First- and second-order transitions of the escape rate in ferrimagnetic or antiferromagnetic particles

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(Received )

Abstract

Quantum-classical escape-rate transition has been studied for two general forms of magnetic anisotropy in ferrimagnetic or antiferromagnetic particles. It is found that the range of the first-order transition is greatly reduced as the system becomes ferrimagnetic and there is no first-order transition in almost compensated antiferromagnetic particles. These features can be tested experimentally in nanomagnets like molecular magnets.

75.50.Xx, 75.45.+j, 03.65.Sq
Understanding the mechanism of transition between two states in a bistable system is of utmost importance of the fast-growing area of macroscopic quantum phenomena (MQP). The rf SQUID and the closely related current-biased Josephson junction have been typical examples of MQP. In recent years, as another good candidates for MQP, small magnetic particles have been investigated via quantum tunneling of magnetization. In general, transition between two states can occur due to two mechanisms. At sufficiently high temperature the transition rate $\Gamma$ obeys the Arrhenius laws, $\Gamma \sim \exp(-U/k_B T)$, with $U$ being the height of the energy barrier. At a temperature low enough to ignore the thermal fluctuation quantum tunneling is relevant with $\Gamma \sim \exp(-U/\hbar \omega)$ where $\omega$ is the oscillation frequency in the well. Thus, the crossover temperature $T_0$ is expected to exist between the thermal activation and quantum tunneling. Whether the two regimes smoothly join or not has been intensive subject over the past few years.

The criterion of first- or second-order transitions for the escape rate has been suggested by Chudnovsky, who showed that if the oscillation period $\tau(E)$ of the instanton is monotonic (nonmonotonic) function where $E$ is the energy of the instanton, $d\Gamma(T)/dT$ becomes continuous (discontinuous), i.e., the second- (the first-) order transition around the crossover temperature. Since then, Gorokhov and Blatter carried out the nonlinear perturbation near the top of the barrier, obtained a criterion for the first-order transition in tunneling problem based on Ref. 4, and applied it to the phase transition of vortex creep pinned in the columnar defect. Later, theoretical investigations for the transition in spin systems have been performed by several groups. Until now theoretical studies have been focused on the ferromagnetic particle. However, considering that most ferromagnetic systems are actually ferrimagnetic particles, the strong exchange interaction should be taken into consideration. The exchange interactions are expected to suppress the first-order transition, and thereby, if it is large, there may be no first-order transition. Thus, it is clearly desirable to assess its importance for the phase transition before contemplating real experiment. Indeed, the exchange interaction in the Hamiltonian does not permit a simple mapping onto the particle problem and the periodic instantons in the reduced one-dimension.
None of such previous theoretical methods are applicable to the present spin system with the exchange interaction. In this paper we will develop new approach to treat the phase transition in ferrimagnetic or antiferromagnetic particles based on the spin-coherent-state path integral, and present complete analytic results of the phase boundary between first- and second-order transitions for two general forms of the magnetic anisotropy energy. Also, we will discuss effects of the fourth order anisotropy in the Hamiltonian on the phase transition in molecular clusters. [10]

Let us consider a small ferrimagnetic or antiferromagnetic particle with two magnetic sublattices whose magnetizations, \( \mathbf{m}_1 \) and \( \mathbf{m}_2 \), are coupled by the strong exchange interaction \( \mathbf{m}_1 \cdot \mathbf{m}_2 / \chi_\perp \), where \( \chi_\perp \) is the perpendicular susceptibility. In the case of a non-compensation of sublattices with \( m(= m_1 - m_2 > 0) \), the Euclidean action can be taken to be

\[
S_E(\theta, \phi) = V \int d\tau \left( \frac{i m_1 + m_2}{\gamma} \dot{\phi} - i \frac{m_1}{\gamma} \phi \cos \theta + \mathcal{L}_{1E} \right),
\]  

(1)

where \( V \) is a volume of the particle, \( \gamma \) the gyromagnetic ratio, and \( \theta, \phi \) spherical coordinates of sublattice magnetization \( \mathbf{m}_1 \) which determines the direction of the Néel vector. Here, \( \mathcal{L}_{1E} \) is the Euclidean Lagrangian density which is composed of the exchange interaction, the anisotropy energy and the energy given by an external magnetic field. The first term in the action \( [11] \) known as the topological term \( [12] \) generates the phase factor related with quantum phase interference. In this work we do not include this term because it is not the purpose of this paper to discuss this issue.

In the simplest easy-axis anisotropy along the \( z \)-axis and a transverse magnetic field along the \( x \)-axis the Euclidean Lagrangian density is expressed as \( [13] \)

\[
\mathcal{L}_{1E} = \frac{\tilde{\chi}_\perp}{2\gamma^2} \left[ (\dot{\theta} + i\gamma H \sin \phi)^2 + (\dot{\phi} \sin \theta + i\gamma H \cos \theta \cos \phi)^2 \right]
+ K_\parallel \sin^2 \theta - mH \sin \theta \cos \phi,
\]

(2)

where \( \tilde{\chi}_\perp = \chi_\perp (m_2/m_1) \). Then, the corresponding classical trajectory is determined by the equations

\[
- i n_\alpha \dot{\phi} \sin \theta + x_\alpha \ddot{\phi} - \frac{1}{2} \dot{\phi}^2 \sin 2\theta + 2ib \dot{\phi} \cos \phi \sin^2 \theta
\]
\[-\frac{1}{2}b^2 \sin 2\theta \cos^2 \phi - 2 \cos \theta (\sin \theta - h \cos \phi) = 0, \tag{3}\]

\[i n_u \dot{\theta} + x_u [\ddot{\phi} \sin \theta + 2 \dot{\phi} \dot{\theta} \cos \theta - 2ib \dot{\theta} \cos \sin \theta \]
\[+ \frac{1}{2}b^2 \sin 2\phi] - 2h \sin \phi = 0. \tag{4}\]

where we have introduced \(m/(K || \gamma) = n_u, \chi_{\perp}/(K || \gamma^2) = x_u, \gamma H = b, H/H_c = h, \) and \(H_c = 2K || /m.\) Note that \(H_c\) is the critical magnetic field at which the barrier vanishes. In this case we decompose \(\theta (\phi)\) into the position of the top of the barrier \(\bar{\theta} (\bar{\phi})\) and a fluctuation term \(\delta \theta (\delta \phi), i.e., \theta = \bar{\theta} + \delta \theta (\phi = \bar{\phi} + \delta \phi)\) for the behavior of the weakly time-dependent solutions, where \(\bar{\theta} = \pi/2\) and \(\bar{\phi} = 0.\) Our goal is to solve Eqs. (3) and (4) for \(\delta \theta(\tau)\) and \(\delta \phi(\tau)\) and find the correction to the oscillation period away from the thermal saddle point.

\[\delta \Omega(\tau) \equiv (\delta \theta(\tau), \delta \phi(\tau)),\] we have \(\delta \Omega(\tau + \beta h) = \delta \Omega(\tau)\) at finite temperature and write it as Fourier series \(\delta \Omega(\tau) = \sum_{n=-\infty}^{\infty} \delta \Omega_n \exp(i\omega_n \tau)\) where \(\omega_n = 2\pi n / \beta h.\) Since simple analysis shows that \(\delta \theta\) is real and \(\delta \phi\) imaginary in this model, to lowest order we write them in the form \(\delta \theta \simeq a\theta u_1 \cos(\omega \tau)\) and \(\delta \phi \simeq i a\phi u_1 \sin(\omega \tau)\) in the vicinity of the thermal saddle-point solution. Here we have parametrized the solutions of the equation of motion by the amplitude \(a\) of the oscillations, which quantifies the difference between the thermal and the time-dependent solutions near the top of the barrier.

Substituting them into Eqs. (3) and (4), we obtain the relation

\[\frac{\phi u_1}{\theta u_1} = \frac{x_u (\omega_{u\pm}^2 - b^2) - 2 + 2h}{-\tilde{n}_u \omega_{u\pm}} = \frac{-\tilde{n}_u \omega_{u\pm}}{x_u (\omega_{u\pm}^2 - b^2) + 2h}, \tag{5}\]

where \(\tilde{n}_u = n_u - 2bx_u,\) and the oscillation frequency

\[\omega_{u\pm}^2 = b^2 - \frac{\tilde{n}_u^2 - 2(1 - 2h)x_u}{2x_u^2} \pm \sqrt{[\tilde{n}_u^2 - 2(1 - 2h)x_u]^2 + 16h(1 - h)x_u^2 - 4b\tilde{n}_u^2 x_u^2} \tag{6}\]

In order to see the behavior of the oscillation period via the frequency we need to investigate Eqs. (3) and (4) by writing \(\delta \theta \simeq a\theta u_1 \cos(\omega \tau) + \delta \theta_2\) and \(\delta \phi \simeq i a\phi u_1 \sin(\omega \tau) + i \delta \phi_2,\) where \(\delta \theta_2\) and \(\delta \phi_2\) are \(O(a^2).\) Neglecting terms of order higher than \(a^2,\) we find \(\omega = \omega_{u+}, \delta \theta_2 = 0,\) and \(\delta \phi_2 = 0.\) This implies that there is no shift in the oscillation frequency. Thus, to third
order in perturbation theory we use \( \delta \theta \simeq a \theta u \cos(\omega \tau) + \delta \theta_3 \) and \( \delta \phi \simeq i a \phi u \sin(\omega \tau) + i \delta \phi_3 \), where \( \delta \theta_3 \) and \( \delta \phi_3 \) are \( O(a^3) \). Substituting them into Eqs. (3) and (4), and neglecting terms of order higher than \( a^3 \), we obtain for the change of the oscillation frequency

\[
\frac{n_u^4 y_u^2}{g_u(h, y_u)}(\omega^2 - \omega_{u+}^2)(\omega^2 - \omega_{u-}^2) = a^2 \theta u_1^2 \frac{\theta u_1}{4} g_u(h, y_u).
\]

(7)

Here \( y_u = x_u/n_u^2 (= \tilde{\chi}_\perp K||/m^2) \) indicates the relative magnitude of the noncompensation. For large noncompensation \( (y_u \ll 1, \text{i.e., } m \gg \sqrt{\tilde{\chi}_\perp K||}) \) and for small noncompensation \( (y_u \gg 1, \text{i.e., } m \ll \sqrt{\tilde{\chi}_\perp K||}) \), the system becomes ferromagnetic and nearly compensated antiferromagnetic, respectively. Without any approximation, \( g_u(h, y_u) \) in Eq. (4) is so complicated that it is not illuminating to present its specific form. Noting that the first-order region is expected to shrink by increasing \( y_u \), it is slightly influenced by the magnetic field terms in the exchange interaction of Eq. (2). Thus, neglecting those terms in the exchange interaction, we can obtain the analytic form of \( g_u(h, y_u) \) approximaterly given by

\[
g_u(h, y_u) \simeq \frac{1}{y^2} [2 - 2y + 12hy - 3y^2 + 8hy^2 - 2y^3 - (2 + 2y + 4hy - y^2)\sqrt{1 - 4y + 8hy + 4y^2}].
\]

(8)

As shown by Chudnovsky, [4] if the oscillation period \( \tau \) is not a monotonic function of \( a \) where \( a \) is a function of \( E \) in the absence of dissipation, the system exhibits a first-order transition. Thus, the period \( \tau(= 2\pi/\omega) \) in Eq. (7) should be less than \( \tau_{u+}(= 2\pi/\omega_{u+}) \), i.e., \( \omega > \omega_{u+} \) for the first-order transition. It implies that \( g_u(h, y_u) > 0 \) in Eq. (4) for the first-order transition, and \( g_u(h, y_u) = 0 \) determines the phase boundary between the first- and the second-order transition. Using Eq. (8), we approximaterly get the phase boundary

\[
\frac{h(y_u)}{y_u} \simeq \frac{2 + y_u}{6} - \frac{12 + 20y_u + 44y_u^2 - y_u^3}{12 f(y_u)^{1/3}} + \frac{f(y_u)^{1/3}}{12 y_u},
\]

(9)

where

\[
f(y) = -18y^2 - 350y^3 - 372y^4 + 66y^5 - y^6
\]

\[
+6\sqrt{3y^3(1 + 3y + y^2)^2(16 - 13y + 328y^2 - 6y^3)}.
\]

(10)
Also, in order to compare Eq. (9) with the phase boundary from the exact calculation, we have employed the numerical method for the exact phase boundary, whose results are illustrated in Fig. 1. The approximate result (9) is found to be slightly different from the exact one obtained by the numerical methods. The scaled magnetic field, $h$ for the phase boundary decreases linearly for $y_u \ll 1$, as $h \approx 1/4 - y_u$ and parabolically for $y_u \lesssim 1/2$, as $h \approx 0.397(y_u - 1/2)^2$. Thus, it is evident that the region for the first order transition is greatly reduced as the system becomes ferrimagnetic and there is no first-order transition in almost compensated antiferromagnetic particles.

We now turn to the biaxial symmetry with the Euclidean Lagrangian density

$$\mathcal{L}_{1E} = \frac{\tilde{\chi}_\perp}{2\gamma^2} \left[ \dot{\phi}^2 + (\phi \sin \theta)^2 \right] + K_1 \cos^2 \theta + K_2 \sin^2 \theta \sin^2 \phi, \quad (11)$$

where $K_1 > K_2 > 0$ are the anisotropy constants. This model describes a hard axis $z$ and an easy axis $x$, and the corresponding classical trajectory satisfies

$$-im_b \dot{\phi} \sin \theta + x_b \left( \ddot{\theta} - \frac{1}{2} \dot{\phi}^2 \sin 2\theta \right) + \sin 2\theta (1 - k \sin^2 \phi) = 0, \quad (12)$$

$$in_b \dot{\phi} + x_b \left( \ddot{\phi} \sin \theta + 2\dot{\phi} \dot{\theta} \cos \theta \right) - 2k \sin \theta \sin \phi \cos \phi = 0. \quad (13)$$

where we have introduced $m/(K_1 \gamma) = n_b$, $\tilde{\chi}_\perp/(K_1 \gamma^2) = x_b$, and $K_2/K_1 = k$. In the high temperature regime the solution of Eqs. (12) and (13) is $\bar{\theta} = \bar{\phi} = \pi/2$. In order to find the order of the transition, let us expand Eqs. (12) and (13) into a series around this solution, as $\theta = \pi/2 + \delta \theta$ and $\phi = \pi/2 + \delta \phi$. Simple analysis for Eqs. (11)-(13) shows that $\delta \theta$ is imaginary and $\delta \phi$ real. Thus, to lowest order in perturbation theory, we write $\delta \theta \simeq ia \theta_{b1} \sin(\omega \tau)$ and $\delta \phi \simeq a \phi_{b1} \cos(\omega \tau)$. Substituting them into Eqs. (12) and (13) while neglecting terms of order higher than $a$, we have

$$\frac{\phi_{b1}}{\theta_{b1}} = \frac{x_b \omega_{b\pm}^2 + 2(1 - k)}{n_b \omega_{b\pm}} = -\frac{n_b \omega_{b\pm}}{x_b \omega_{b\pm}^2 - 2k} \quad (14)$$
and the oscillation frequency

\[
\omega_{b \pm}^2 = -\frac{n_b^2}{2x_b^2} + 2(1 - 2k)x_b \pm \sqrt{\frac{n_b^4 + 4(1 - 2k)n_b^2x_b + 4x_b^2}{2x_b^2}}.
\tag{15}
\]

Next, let us write \(\delta \theta \simeq ia\theta_1 \sin(\omega \tau) + i\delta \theta_2\), and \(\delta \phi \simeq a\phi_1 \cos(\omega \tau) + \delta \phi_2\), where \(\delta \theta_2\) and \(\delta \phi_2\) are of the order of \(a^2\). Inserting them into Eqs. (12) and (13), we arrive at \(\omega = \omega_{b \pm}\) and \(\delta \theta_2 = \delta \phi_2 = 0\). In order to find the change of the oscillation period, we proceed to the third order of perturbation theory by writing \(\delta \theta \simeq ia\theta_1 \sin(\omega \tau) + i\delta \theta_3\), and \(\delta \phi \simeq a\phi_1 \cos(\omega \tau) + \delta \phi_3\). Substituting them again into Eqs. (12) and (13) and retaining only terms up to \(O(a^3)\), we have

\[
n_b^4y_b^2(\omega^2 - \omega_{b+}^2)(\omega^2 - \omega_{b-}^2) = a^2\frac{\phi_{b1}^2}{4}g_b(k, y_b),
\tag{16}
\]

where \(y_b = x_b/n_b^2 = \tilde{\chi}_\perp K_1/m^2\) and

\[
g_b(k, y) = \frac{2}{y^2}[1 + 3y - 4ky - 4y^3 - (1 + y - 2y^2)\sqrt{1 + 4y - 8ky + 4y^2}].
\tag{17}
\]

Here we note that the parameter \(y_b\) has the same physical meaning as \(y_u\) in uniaxial symmetry by replacing \(K_\parallel\) by \(K_1\). Continuing in the present case as in the earlier model we have \(g_b(k, y_b) > 0\) for the first-order transition and the phase boundary given by

\[
k = \frac{1}{2}(1 - y_b)(1 + 2y_b)^2.
\tag{18}
\]

As follows from Fig. 2, the criterion [7] that in case of the biaxial symmetry the first-order transition occurs at \(k > 1/2\) is not valid in ferrimagnetic particles. Fig. 2 shows that the ratio of two anisotropy constants, \(k\) increases linearly for \(y_b \ll 1\), as \(k \simeq (1 + 3y_b)/2\) and has a maximum at \(y_b = 1/2\). Therefore, the region for the first-order transition is greatly suppressed with increasing \(y_b\) and vanishes beyond \(y_b = 1/2\).

To illustrate the above results with concrete examples we discuss two molecular clusters, \(\text{Mn}_{12}\) and \(\text{Fe}_8\). Actually, both samples are ferrimagnetic, and thereby \(y_u\) and \(y_b\) should be
taken into account in uniaxial and biaxial symmetry, respectively. Taking the measured value of the anisotropy parameter, e.g., \( k = 0.728 \) for Fe\(_8\), it is seen from Fig. 2 that the system may exhibit the first-order transition for \( y_b \lesssim 0.157 \) and the second-order transition beyond that region. This point should be checked in experiment. Also, since neutron scattering data \(^{10}\) shows that an Fe\(_8\) (Mn\(_{12}\)) should be described by the biaxial (uniaxial) spin Hamiltonian with the fourth order anisotropy term, it is meaningful to discuss how much it makes an effect on the phase transition. Our analysis shows that the first-order region is slightly reduced by adding the fourth order terms in the Hamiltonian. Taking Fe\(_8\) for instance, the range of \( y_b \) for the first-order transition is changed to \( 0 \leq y_b \lesssim 0.153 \), as shown in Fig. 3. Thus, considering the fact that most ferromagnetic systems are ferrimagnetic, it is very important to obtain the information on the magnitude of the quantities \( y_u \) and \( y_b \) for observing the first-order transition in real experiments.

In conclusion, we have presented the phase diagrams for first- and second-order transitions in ferrimagnetic or antiferromagnetic particles. It is found that the range of the first-order transition is greatly suppressed by the exchange enhancement. In fact, this can be qualitatively understood from the consideration that the exchange interaction produces some effective magnetic field and thereby plays an important role in reducing the range of the first-order transition. In this respect, the first-order transition can not be observed in almost compensated antiferromagnetic particles, which is consistent with our analytic results. This general features is expected to be observable in nanomagnets including molecular clusters.

Discussions with D. A. Gorokhov, W. Wernsdorfer and B. Barbara are acknowledged. This work was supported by the Korea Research Foundation Grant (KRF-99-041-D00188)
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FIGURES

FIG. 1. Phase diagram $h(= H/H_c)$ vs $y_u(= \tilde{\chi}_{\perp} K_{||}/m^2)$ obtained by the exact calculation for the uniaxial symmetry in a transverse magnetic field. Note that $h$ and $y_u$ contain information of the magnetic field and the relative noncompensation, respectively, and thereby the system tends to be ferrimagnetic or antiferromagnetic with increasing $y_u$. See the text for details. Inset: Comparison of the exact result (a) with the approximate one (b).

FIG. 2. Phase diagram $k(= K_2/K_1)$ vs $y_b(= \tilde{\chi}_{\perp} K_1/m^2)$ for the transition in biaxial symmetry. Note that $k$ contains information of the relative strength of the biaxial two axes, and the first-order transition is expected for $k \lesssim 1$ in which the system starts to be biaxial from uniaxial. Also, the parameter $y_b$ has the same physical meaning as $y_u$ in uniaxial symmetry. See the text for details.

FIG. 3. Change of the range of the first-order transition for the biaxial spin Hamiltonian in Fe$_8$ (a) with and (b) without the fourth order anisotropy term in the Hamiltonian. Note that (a) $0 < y_b \lesssim 0.153$ and (b) $0 < y_b \lesssim 0.157$ for the first-order transition.
