PHYSICAL REVIEW B **85**, 184409 (2012)

Harmonic transition-state theory of thermal spin transitions

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(Received 14 November 2011; revised manuscript received 17 February 2012; published 9 May 2012)

A rate theory for thermally activated transitions in spin systems is presented. It is based on a transition-state approximation derived from Landau-Lifshitz equations of motion and quadratic expansion of the energy surface at minima and first order saddle points. While the flux out of the initial state vanishes at first order saddle points, the integrated flux over the hyperplanar transition state is nonzero and gives a rate estimate in good agreement with direct dynamical simulations of test systems over a range in damping constant. The preexponential factor obtained for transitions in model systems representing nanoclusters with 3 to 139 transition metal adatoms is on the order of 10^{11} to 10^{13} s^{-1}, similar to that of atomic rearrangements.

DOI: 10.1103/PhysRevB.85.184409 PACS number(s): 05.20.Dd, 75.10.−b

I. INTRODUCTION

Metastable magnetic states have been studied experimentally in small systems of various kinds, in particular, molecular magnets[1] and supported[2–4] and free-standing[5] transition metal clusters. The stability of such states with respect to thermal fluctuations is an important issue in many contexts, for example, when assessing the limit to which magnetic recording devices can be miniaturized. Although the systems mentioned above are quite different, they are all characterized by two or more magnetic states which correspond to different orientations and/or different values of the magnetic moments. A preparation of a system in a particular magnetic state can be destroyed by thermally activated transitions to other states. For long-lived magnetic states, the separation in time scale between fast precession of magnetic moments and slow transitions between states make direct dynamical simulation of spin dynamics[6] impractical. This, however, opens the possibility for the use of a statistical approach for estimating spin transition rates as well as determining the transition mechanism. Statistical approaches have been presented previously for a single macrospin,[7,8] but we are not aware of a previous presentation of a statistical rate theory for systems with multiple spins. Even in small clusters, transitions can involve nucleation and propagation of a domain wall rather than coherent rotation of magnetic moments.[2,3] A macrospin approximation would in such cases give the wrong activation barrier height and a poor estimate of the rate. In this paper, a method for finding the mechanism and rate of thermal spin transitions is developed by adapting transition state theory (TST)[9] to multiple spin degrees of freedom. It gives an Arrhenius law for the transition rate, which can be evaluated using only the input that would be needed for a direct simulation of the spin dynamics—a simulation that would, however, be impossibly long in the cases of interest.

II. THEORY

TST[9] has been used extensively for estimating the rate of thermally activated atomic rearrangements such as chemical reactions and diffusion.[10] The separation of time scale mentioned above makes it possible to estimate the rate from the probability of finding the system in the most restrictive and least likely region separating the initial state from possible final states—the transition state. Given a transition state dividing surface, $f(\boldsymbol{x}) = 0$, where $\boldsymbol{x}$ represents all dynamical variables in the system, the reaction rate constant, k^{TST}, can be estimated for spin systems in a way that is analogous to atomic systems[11] as

$$k^{\mathrm{TST}} = \frac{1}{C}\int_R e^{-E(\boldsymbol{x})/k_BT}\,\delta\,[f(\boldsymbol{x})]\,v_\perp(\boldsymbol{x}) \times H\,[v_\perp(\boldsymbol{x})]\,J(\boldsymbol{x})\prod_i dx_i, \tag{1}$$

where R denotes the region associated with the initial state up to and including the dividing surface, $J(\boldsymbol{x})$ is a Jacobian determinant, E is the energy of the system, $v_\perp(\boldsymbol{x}) = \nabla f(\boldsymbol{x})\cdot\dot{\boldsymbol{x}}$ is a projection of the velocity onto the normal of the dividing surface, and C is a normalization constant given by

$$C = \int_R e^{-E(\boldsymbol{x})/k_BT} J(\boldsymbol{x})\prod_i dx_i.$$

A central approximation is that a trajectory only crosses the dividing surface once,[12] and this is taken into account by inserting a Heaviside step function H into Eq. (1). For spin systems, the relevant variables are taken to be spherical angles θ_i and ϕ_i defining the direction of the ith magnetic moment. The set of variables for a system of spins is denoted as $\boldsymbol{x} \equiv \{\boldsymbol{\theta},\boldsymbol{\phi}\} \equiv \{\theta_1,\theta_2,\ldots,\theta_N,\phi_1,\phi_2,\ldots,\phi_N\}$. The magnitude of the magnetic moments M_i is assumed to be a function of the angles, $M_i(\boldsymbol{\theta},\boldsymbol{\phi})$, i.e., an adiabatic approximation is invoked. The Jacobian determinant is then $J(\boldsymbol{\theta},\boldsymbol{\phi}) \equiv \prod_i M_i^2(\boldsymbol{\theta},\boldsymbol{\phi})\sin\theta_i$.

The normal projection of the velocity, $v_\perp(\boldsymbol{\theta},\boldsymbol{\phi})$, needs to be estimated at each point on the dividing surface. The equation of motion is taken to be the Landau-Lifshitz equation (see Ref. 13)

$$\frac{d\boldsymbol{M}_i}{dt} = \gamma\boldsymbol{M}_i \times \frac{\partial E}{\partial \boldsymbol{M}_i}, \tag{2}$$

where γ is a gyromagnetic ratio. In the adiabatic limit, this equation can be split into two equations:

$$\dot{\phi}_i = \frac{\gamma}{M_i\sin\theta_i}\frac{\partial E}{\partial\theta_i} \quad\text{and}\quad \dot{\theta}_i = -\frac{\gamma}{M_i\sin\theta_i}\frac{\partial E}{\partial\phi_i}. \tag{3}$$

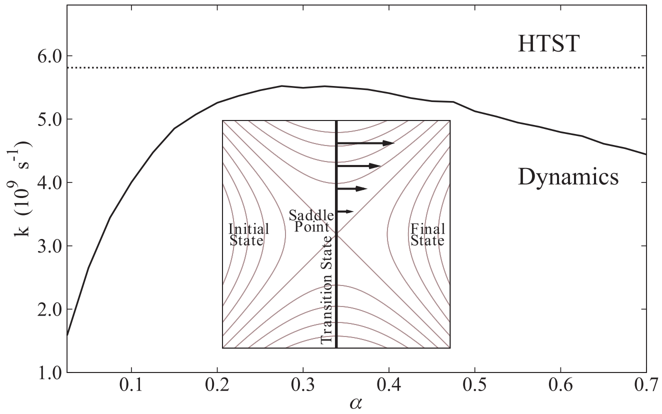

FIG. 1. Comparison of the rate of transitions in a spin trimer obtained directly from dynamics given by the Landau-Lifschitz-Gilbert equation of motion as a function of the damping constant α at $T = 23$ K (solid line) and a harmonic TST estimate (dotted line). *Inset:* the energy surface near a first order saddle point, representation of a hyperplanar transition state dividing surface (thick line) and the spin velocity (arrows).

The length of the velocity vector is proportional to the magnitude of the energy gradient but the velocity and gradient vectors are perpendicular.

The TST expression for the rate constant can be simplified by introducing quadratic approximations to the energy surface around the critical points to give a harmonic TST (HTST) approximation. The transition state dividing surface is then chosen to be a hyperplane going through a first order saddle point on the energy ridge separating the initial state from product states (see Fig. 1). The hyperplane normal is chosen to point in the direction of the unstable mode, the eigenvector of the Hessian matrix along which the saddle point is a maximum. If second order saddle points on the ridge are high enough above first order saddle points, then each first order saddle point corresponds to a specific transition mechanism and a certain product state. For each possible final state, one or more minimum energy paths (MEP) can be found. Following an MEP means advancing each degree of freedom of the system in such a way that the energy is minimal with respect to all degrees of freedom perpendicular to the path. The nudged elastic band (NEB) method[14] can be used to find MEPs between a given pair of initial and final states. A maximum along an MEP corresponds to a first order saddle point on the energy surface and the highest one gives an estimate of the activation energy.

Unlike atomic systems, the velocity in spin systems is zero at a saddle point because the gradient is zero. In the vicinity of the saddle point, the energy surface, $E(\boldsymbol{\theta},\boldsymbol{\phi})$, can in general be approximated as a parabolic function and the magnitude of the energy gradient and, thereby, the velocity increases as one moves away from the saddle point. Moreover, since the energy gradient lies within the dividing surface at points on the dividing surface, the velocity is perpendicular to the dividing surface.

The expansion of the energy at the minimum ($\beta = m$) and at the saddle point ($\beta = s$) is

$$E_\beta(\boldsymbol{q}) = E_\beta(0) + \frac{1}{2}\sum_{j=1}^{D} \epsilon_{\beta,j} q_{\beta,j}^2, \tag{4}$$

where D is twice the number of spins. The expansion is in terms of normal mode coordinates, displacements along eigenvectors of the Hessian matrix. The Landau-Lifshitz equations become linear with this quadratic approximation to the energy surface. At the saddle point, one of the eigenvectors, the one corresponding to the unstable mode, is orthogonal to the dividing surface. Labeling this mode as $q_{s,1}$, the velocity $v_\perp(\boldsymbol{\theta},\boldsymbol{\phi}) = \dot{q}_{s,1}$ can according to Eqs. (2)–(4) be written as a linear combination of normal mode coordinates,

$$v_\perp = \sum_{i=2}^{D} a_i q_{s,i}. \tag{5}$$

The direction of each eigenvector at the saddle point is chosen so that $a_i > 0$ leads to a positive contribution to $v_\perp$, i.e., pointing away from the initial state.

With these quadratic approximations to the energy surface, the HTST expression for the rate constant becomes

$$k^{\mathrm{HTST}} = \frac{\int e^{-\sum_{j=2}^{D} \epsilon_{s,j} q_{s,j}^2/2k_BT} \sum_{i=2}^{D} a_i q_i dq_2 \dots dq_D}{\int e^{-\sum_{j=1}^{D} \epsilon_{m,j} q_{m,j}^2/2k_BT} dq_1 \dots dq_D} \times \frac{J_s}{J_m} e^{-(E^s - E^m)/k_BT}, \tag{6}$$

where $J_\beta \equiv J(\boldsymbol{\theta}^\beta,\boldsymbol{\phi}^\beta)$. The denominator is simply a product of Gaussian integrals. The numerator is more complicated because the integrals involved are carried out over the region where $v_\perp \geqslant 0$, i.e., over the half-plane $a_2 q_2 + a_3 q_3 + \dots + a_D q_D \geqslant 0$. After some algebra (which will be published elsewhere) one obtains

$$k^{\mathrm{HTST}} = \frac{1}{2\pi} \frac{J_s}{J_m} \sqrt{\sum_{j=2}^{D} \frac{a_j^2}{\epsilon_{s,j}}} \frac{\prod_{i=1}^{D} \sqrt{\epsilon_{m,i}}}{\prod_{i=2}^{D} \sqrt{\epsilon_{s,i}}} e^{-(E^s - E^m)/k_BT}, \tag{7}$$

which agrees with an Arrhenius expression with an activation energy $E_a = E^s - E^m$ and a temperature independent preexponential, ν.

The theory presented here is classical and makes use of harmonic approximations to the energy surface. An extension to full transition-state theory involving statistical sampling within the dividing surface as well as the inclusion of quantum tunneling by use of Feynman path integrals, analogous to what has been formulated for particle systems (see, for example, Refs. 15 and 16), is an ongoing project.

III. APPLICATIONS

Below, this rate theory is applied to transitions in three different systems. First, three spins are considered and HTST results compared with direct simulations of the dynamics. Then, the method is applied to a cluster of 139 Fe adatoms on a W(110) surface. These first two systems are described by a Heisenberg-type Hamiltonian. The third example is a three atom Fe cluster on a substrate described by a Alexander-Anderson Hamiltonian for itinerant electrons.

The Heisenberg-type Hamiltonian can be written in a general form:

$$E = -\sum_n K_n \sum_i (\boldsymbol{M}_i \cdot \boldsymbol{e}_n)^2 - \frac{1}{2} J \sum_{\langle i,j \rangle} \boldsymbol{M}_i \cdot \boldsymbol{M}_j - D \sum_{i \neq j} \frac{3(\boldsymbol{r}_{ij} \cdot \boldsymbol{M}_i)(\boldsymbol{r}_{ij} \cdot \boldsymbol{M}_j) - r_{ij}^2 (\boldsymbol{M}_i \cdot \boldsymbol{M}_j)}{r_{ij}^5}. \qquad (8)$$

The magnitude of the magnetic moments M_i is independent of angles. The first term represents anisotropy, J denotes the exchange coupling, D is dipolar coupling constant, and $\boldsymbol{r}_{ij}$ is the vector between sites i and j. Exchange interaction is only between nearest neighbors (indicated by the angular brackets).

The HTST rate constant estimate, Eq. (7), was tested by comparing it with the rate of transitions observed in a direct simulation of the dynamics of a multidimensional system involving three spins which are coupled through the exchange interaction. Parameters of the Hamiltonian [Eq. (8)] were chosen to include easy-axis $K_\perp$ and easy-plane $K_\parallel$ anisotropies which could result from the interaction with a substrate. As a result, minima and saddle points are formed on the energy surface. Parameter values and temperature were chosen so as to make the transitions frequent enough to obtain good statistics in dynamics simulations spanning a long time interval but infrequent enough for the system to be able to thermalize at the bath temperature in between transitions. The parameters were $M = 2.7\mu_B$, $K_\perp M^2 = 5$ meV, $K_\parallel M^2 = -10$ meV, and $JM^2 = 15$ meV. Two equivalent minima exist on the energy surface: at $\theta_i = \pi/2$ and $\phi_i = \{\pi/2, 3\pi/2\}$. There are two equivalent saddle points between the minima: at $\theta_i = \pi/2$ and $\phi_i = \{0, \pi\}$. The activation energy was found to be $E_s - E_m = 15$ meV. The dynamics of the spins were calculated numerically from the Landau-Lifshitz-Gilbert equations where dissipation and random force terms are included to couple the spins to a thermal heat bath.[17,18] Long simulations were performed, spanning 10^{-5} s and 10^9 steps at a temperature of 23 K. This gave satisfactory statistics in the counting of transitions. The dynamical simulations were carried out for various values of the damping constant, α, as shown in Fig. 1. The agreement with the HTST estimate is good, within a factor of 2, for a wide range in the damping constant. While the parameters and temperature have been chosen here to make it possible to obtain the transition rate from direct simulation of the spin dynamics, the usefulness of the rate theory presented here becomes clear when the temperature is lowered, the activation energy barrier increased, and/or the number of spins increased. Then, the direct calculation become difficult, or even impossible, while the evaluation of the rate expression remains relatively straightforward.

To demonstrate the methodology presented here on a more challenging system, we applied it to a larger, rectangular island of 139 Fe atoms (see Fig. 2). The parameters in Eq. (8) were chosen to mimic roughly Fe on W(110) substrate:[2,19] dipole-dipole interactions were included as well as anisotropy in the $[1\bar{1}0]$ direction (which is perpendicular to the long axis of the cluster) resulting from the interaction with the substrate. The parameter values were $KM^2 = 0.55$ meV, $JM^2 = 12.8$ meV,[2] and $D/J = 10^{-3}$.[19] Two degenerate states with spins parallel to the anisotropy axis represent the most stable states. A NEB calculation starting from a uniform rotation revealed a more complicated transition mechanism involving a metastable intermediate state, as shown in Fig. 2. The metastable state can be seen as the emergence of a new domain,

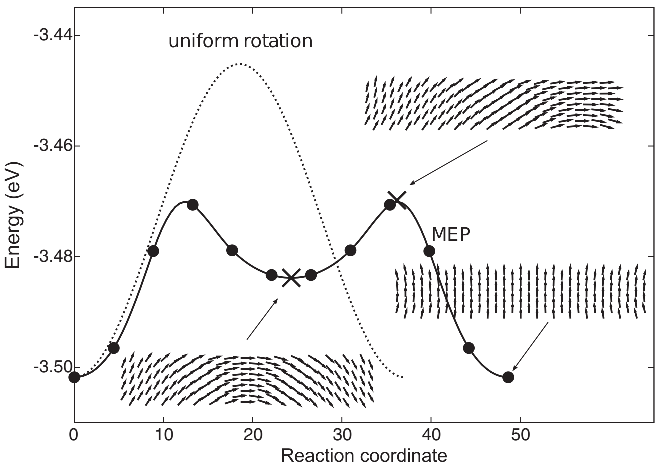

FIG. 2. Minimum energy path (solid line) for a magnetic transition in a rectangular shaped 139 Fe atom island on W(110) surface. A relaxation starting from a straight line interpolation (dotted line) representing a uniform rotation of the spins between spin up and spin down states revealed an intermediate metastable state, as shown by the insets. The discretization points used in the NEB calculation are shown with filled circles but the minimum for the metastable state and a saddle point obtained by subsequent optimization are marked with X. *Insets:* noncollinear spin configurations at various points along the path.

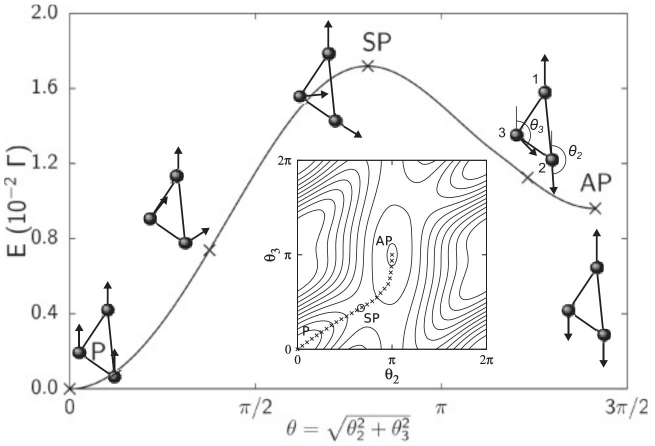

FIG. 3. Minimum energy path for a transition between a parallel (P) and antiparallel (AP) state of a Fe trimer on a metal substrate described with the Alexander-Anderson model. Spin configurations corresponding to locations marked with X on the path are shown with arrows denoting magnitude and direction of the magnetic moments. The direction of spin 1 is taken to be fixed but the relative angles, θ_2 and θ_3, are variable. The energy is given in units of the d-level width, Γ, due to s-d hybridization. *Inset:* energy surface showing minima corresponding to P and AP states, and the calculated minimum energy path for the transition. Saddle point (SP) is also shown.

but the cluster is too small for it to form fully. The activation energy for transitions out of the metastable state is 14 meV and the calculated preexponential, according to Eq. (7), is $\nu = 7.4 \times 10^{12}\ \mathrm{s}^{-1}$. The lifetime of the intermediate state can be estimated as $\tau(T) = 1/k^{\mathrm{HTST}}$.

Although the Landau-Lifshitz equation was first formulated in order to describe the precessional motion of classical magnetization, it has proven to be an equation of motion also for quantum systems.[13,20] This expands the range of applicability of the rate theory presented here. We demonstrate this on a triatomic Fe island described within the noncollinear Alexander-Anderson model (see Ref. 21) which captures the main features of magnetic ordering in $3d$ transition metal clusters on a metal surface. In particular, several different magnetic states close in energy have been found for supported trimers of Fe, Cr, and Mn.[21] The question is how large an energy barrier separates these states and how long their lifetime is at a given temperature. While a triatomic island is too small to support long-lived metastable states, we use this as an illustration of the methodology because the energy surface can be visualized easily.

The implementation of the model within a mean field approximation and the parameter values used here to represent Fe trimer are given in Ref. 21. The interaction of d-electrons with the itinerant s- and p-bands is included, but not spin-orbit interaction so spin space and the real space are not connected. There is no energy barrier to uniform rotation of magnetic moments and only relative orientation of spins is relevant. The quantization axis for the system is chosen to be along the magnetic moment of one of the trimer atoms, atom 1. The configuration is then specified by only four degrees of freedom. There are two energy minima and both of them correspond to in-plane orientation of the spins. The global minimum represents a state with parallel (P) magnetic moments, but a metastable state with antiparallel (AP) moments also exists. Figure 3 shows a contour graph of the energy as a function of two angles θ_2 and θ_3, while for all atoms we set $\phi_i = 0$. The minimum energy path between AP and P states turns out to lie in-plane and is also shown in Fig. 3. The activation energy for leaving the metastable state is $E_a = E^{\mathrm{SP}} - E^{\mathrm{AP}} = 0.007\Gamma$, where Γ is the width of the d-level due to s-d hybridization.[21] If $\Gamma = 1$ eV, the calculated preexponential is $\nu = 2.4 \times 10^{11}\ \mathrm{s}^{-1}$. A study of the effect of island size and shape on such metastable states and the rate of transitions between the states is ongoing and the results will be presented at a later time.

ACKNOWLEDGMENTS

This work was supported by The Icelandic Research Fund, Nordic Energy Research, and The University of Iceland Scholarship Fund. We thank Professor Pieter Visscher for several constructive comments on the manuscript and Professor Björgvin Hjörvarsson for stimulating discussions.

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