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A stochastic model for magnetic dynamics in single-molecule magnets

R. López-Ruiz [a,*], P.T. Almeida [a], M.G.F. Vaz [b], M.A. Novak [c], F. Béron [a], K.R. Pirota [a]

[a] Instituto de Física Gleb Wataghin - Universidade Estadual de Campinas, 13083-859 Campinas (SP), Brazil
[b] Instituto de Química, Universidade Federal Fluminense, 24020-150 Niterói (RJ), Brazil
[c] Instituto de Física - Universidade Federal do Rio de Janeiro, 21941-972 Rio de Janeiro (RJ), Brazil

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ABSTRACT

Hysteresis and magnetic relaxation curves were performed on double well potential systems with quantum tunneling possibility via stochastic simulations. Simulation results are compared with experimental ones using the Mn_{12} single-molecule magnet, allowing us to introduce time dependence in the model. Despite being a simple simulation model, it adequately reproduces the phenomenology of a thermally activated quantum tunneling and can be extended to other systems with different parameters. Assuming competition between the reversal modes, thermal (over) and tunneling (across) the anisotropy barrier, a separation of classical and quantum contributions to relaxation time can be obtained.

1. Introduction

Single-molecule magnets (SMMs) [1–4] stand out for their appeal to the research on the foundations of quantum physics as well as promising applications [5,6]. SMMs are metal-organic clusters made of a magnetic core surrounded by an organic ligand shell. They are neutral entities that form molecular crystals bound by weak Van der Waals interactions. However, their basic magnetic properties, i.e., ground-state spin and magnetic anisotropy, are characteristic of the isolated clusters [7–10]. They exhibit hysteresis, i.e., magnetic memory, below a certain temperature [11]. This phenomenon is a signature (equal to nanoparticles, but with the advantage of being monodisperse in size) of the blocked state produced by an anisotropy barrier. The hysteresis observed, however, was found to be rather unconventional, showing steps in the magnetization. The steps are located at those magnetic fields where the magnetic states with opposite spin orientation (i.e. spin-up and spin-down states) become degenerated in energy [12–15]. At these fields, the possibility of crossing the energy barrier U by quantum tunneling provides a kind of short-cut to the classical relaxation process [16–19]. Thus, the hysteresis and, in general, the spin dynamics of SMM, reveal signatures of fascinating quantum phenomena, which result from their very small size and the discreteness of their magnetic energy level scheme (Fig. 1a). In this respect, these systems are ideally suited to investigate the fuzzy borderline between the classical and quantum worlds [20,21].

The theoretical tools to study the magnetic dynamics of SMM are usually based on the solution of the spin Hamiltonian that describes the quantum SMM behavior by numerical methods. In this dissipative system, the spins are mainly coupled to a thermal bath via spin–phonon interactions [22] which are responsible for the time involved in the relaxation process [23]. When quantum tunneling is involved, off-diagonal spin elements different from the classical Pauli-type diagonal counterparts have to be introduced in the $(2S+1)\times(2S+1)$ spin density matrix also introducing a faster scale time. Thus, solving the system on the basis of Sz eigenstates introduces a complexity [24] requiring sophisticated computing tools, sometimes not considering the temperature dependence [25]. On the other hand, stochastic models, usually solved via Monte-Carlo methods, are faster and have been extensively used to study magnetic kinetics on classical superparamagnets [26–28] or in the quantum limit, i.e., very low temperatures where only tunneling spin reversal is allowed [29,30]. The main objective of this work is to extend a purely probabilistic perspective, recently used by our group [31] to simulate SMMs at intermediate temperatures. At a finite temperature, from a thermal equilibrium population, the tunneling spin flip is another possibility at resonance fields. In [31] we have focused on experimental and simulated first-order reversal curve (FORC) diagrams of the Mn_{12} SMM model system [32]. Here, we extend the simulation model to other SMMs through the variation of the physical parameters involved in the system. Since hysteresis origin is the slow time evolution of the magnetization towards the equilibrium, the addition of the field dependence on the magnetic relaxation is a natural improvement. Thus, we have extended the model to simulate the magnetization relaxation curves which also allows us to separate the classical and quantum (tunneling)

* Corresponding author.
E-mail address: rlruiz@ifi.unicamp.br (R. López-Ruiz).

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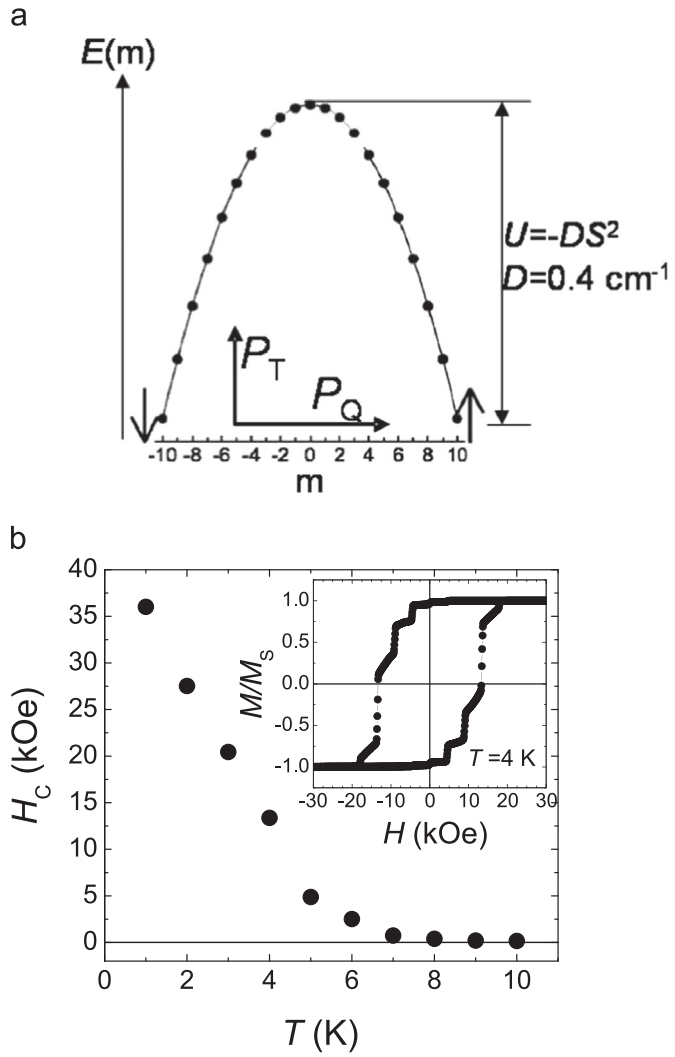

Fig. 1. (a) Energy levels $E(m)$ vs. the quantum number m at $H=0$ for Mn_{12}. It shows a bistable potential for the spin due to the magnetic anisotropy with an energy barrier $U = DS^2$. Fundamental levels represent the "spin down" and "spin up" orientation. The two probabilities taken in account in simulation: "vertical" P_T to populate the excited levels and "horizontal" P_Q to populate the degenerate level across the barrier are indicated. (b) Simulated temperature-dependent coercive field. Inset: Simulated hysteresis curve for $T=4$ K (extracted from [31] only for visual purposes).

contributions [33]. The model provides a very fast zeroth-order approximation to the experimental results that allow us to simulate systems such as ferritin nanoparticles [34,35]. The dynamics come from the directions of the individual spins in the ensemble after a simulation step and not from intrinsic spin dynamics. The difficulty of defining a time scale, that is inherent to Monte Carlo methods, is solved in our work via phenomenology comparison.

The plan of the paper is the following: in Section 2 the two probabilities behind the spin reversal, i.e., to pass through (quantum) or over (classical) the anisotropy barrier in a SMM are introduced and the stochastic simulations to reproduce hysteresis and magnetization relaxation curves explained. Hysteresis simulation results in a Mn_{12} model system are shown in Section 3, generalizing to other SMMs by means of changes in the parameters related to the anisotropy and introducing the time in the simulation. In Section 4, we show magnetization relaxation curves where both classical and quantum contributions to magnetization reversal can be extracted from this competition context. The conclusions and perspectives are summarized in Section 5.

2. Simulation basis

In the framework of these magnetic bistable systems (see Fig. 1a for Mn_{12} example), the simulation model takes into account both thermal and tunneling effects. They are represented by two probabilities, respectively: *vertical* probability of populating the excited levels by effects of the thermal bath perturbation, P_T, and an *horizontal* probability to pass through the barrier by tunneling, P_Q.

2.1. Boltzmann thermal population

The thermal activation probability P_T gives the possibility of a spin to jump from the ground state $m=\pm S$ to an excited level $m = m_T$. Based on a Maxwell–Boltzmann distribution where the number of spins is conserved in time and every spin contributes equally to the macroscopic state, we assume that the population of an excited level is determined by a Boltzmann factor. This probability reads

$$P_T(m_T) = \frac{\exp\left(\frac{E(m=\pm S) - E(m_T)}{k_B T}\right)}{\sum_{m_T=0..\pm S} \exp\left(\frac{E(m=\pm S) - E(m_T)}{k_B T}\right)} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature and the m-level energy $E(m)$ can be calculated by

$$E(m) = -Dm^2 - g\mu_B H_z m \quad (2)$$

where D is the axial zero-field splitting parameter connected to the anisotropy, g is the gyromagnetic factor and μ_B is the Bohr magneton. Eq. (2) represents the effect of the anisotropy at zero field and the Zeeman splitting produced under the application of a bias field H_z. At zero field the energy levels are represented in Fig. 1a for the Mn_{12} model.

2.2. Landau–Zener tunneling probability

The quantum tunneling probability P_Q between the spin levels m and m' of each side of the barrier is calculated in terms of the Landau–Zener theory, i.e., spin inversion can occur due to non-coherent resonance when a crossing field is swept at a constant rate dH_z/dt:

$$P_Q = 1 - \exp\left(\frac{-\pi\Delta^2}{2\hbar g\mu_B(m' - m)dH_z/dt}\right) \quad (3)$$

It strongly depends on the tunnel splitting Δ that can be calculated in the context of the perturbation theory using a chain rule approximation in the quasi-classical limit [16], namely:

$$\Delta = \frac{2D}{((m' - m - 1)!)^2}\sqrt{\frac{(S+m')!(S-m)!}{(S-m')!(S+m)!}}\left(\frac{g\mu_B H_x}{2D}\right)^{|m'-m|} \quad (4)$$

A transversal field H_x is introduced to represent a perturbation perpendicular to the z-axis that mixes the energy levels, allowing tunneling between the m degenerated states. In practice, it is due to non-uniaxial anisotropy terms produced by crystallographic defects and other linear terms from couplings and the non-perfect external field orientation which distorts the purely uniaxial anisotropy.

Summarizing, the spins can invert by two ways: (i) above the barrier if the spin has reached the top of the potential barrier (classical jump) or (ii) crossing the barrier by tunneling when energy m-levels are in resonance (quantum jump).