Self-organized patterns of macroscopic quantum tunneling in molecular magnets

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We study low temperature resonant spin tunneling in molecular magnets induced by a field sweep with account of dipole-dipole interactions. Numerical simulations uncovered formation of self-organized patterns of the magnetization and of the ensuing dipolar field that provide resonant condition inside a finite volume of the crystal. This effect is robust with respect to disorder and should be relevant to the dynamics of the magnetization steps observed in molecular magnets.

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Molecular magnets had become focus of interest after it was demonstrated [1] that a crystal of Mn$_{12}$-Acetate molecules is equivalent to a regular array of single-domain superparamagnetic particles of spin 10. The subsequent discovery of the stepwise hysteresis curve in Mn$_{12}$-Ac [2] made it a model system for the study of macroscopic quantum tunneling of the magnetic moment [3]. In a typical macroscopic experiment the magnetic field is swept at a constant rate, making the spin energy levels affected the size of the magnetization step. In this Letter we develop theoretical framework for understanding the dynamics of the steps. We will be concerned with the regime of pure quantum tunneling or thermally assisted quantum tunneling [4].

It had been recognized in the past [5] that the knowledge of the probability of spin tunneling alone is insufficient to describe the tunneling dynamics of molecular magnets. This is because the reversal of any individual spin changes the long-range dipolar magnetic field of the entire crystal, which tunes other spins in or out of resonance. The tunneling dynamics of a molecular magnet near a resonance is, therefore, non-local and non-linear [6]. Prokof’ev and Stamp [3] suggested that the relaxation could occur near some surface inside the sample which is the locus of points characterized by the zero bias between spin energy levels. Their local model, however, could not capture the evolution of such a surface in time that should occur during magnetic relaxation [7]. Later studies of the collective relaxation in molecular magnets [8,9] did take the non-locality into account. They did not consider, however, the dynamics generated by the field sweep that is important for the formation of a coherent spatial structure in the macroscopic tunneling dynamics driven by dipolar fields.

In this Letter we derive and solve non-linear integro-differential equations that govern the self-organized tunneling dynamics of spins coupled by dipolar interactions.

Let $n_m$ be the normalized population of the $m$-th level, $\sum_m n_m = 1$. In a typical macroscopic experiment one magnetizes the crystal such that initially $n_{-S} = 1$ while populations of other states are zero. The field is then swept in the opposite direction at a constant rate. It has been demonstrated theoretically [10] and confirmed by experiments [11] that in the thermally assisted regime a step in the magnetization curve is dominated by a resonance between particular spin energy levels, see Fig. 1. This resonance is determined by the maximum of $\Delta_{mn,m'} = \exp[-(E_m - E_{-S})/(k_B T)]$, where $\Delta_{mn,m'}$ is the tunnel splitting of the $m$-th and $m'$-th levels, $E_m$ is the energy of the $m$-th level, and $T$ is temperature. On approaching this resonance, the population of the $| - S \rangle$ state satisfies the following equation [4]

$$\dot{n}_{-S} = -\Gamma n_{-S}$$

(1)

where

$$\Gamma = \frac{1}{2} \left( \frac{\Delta_{mn,m'}}{\hbar} \right)^2 \exp\left(-\frac{E_m - E_{-S}}{k_B T}\right) \times \frac{\Gamma_{m,m'}^m}{(W/\hbar)^2 + (\Gamma_{m,m'}^m/2)^2}.$$ 

(2)

Here $W$ is the energy bias between $m$ and $m'$, and $\Gamma_{m,m'} = \Gamma_m + \Gamma_{m'}$, $\Gamma_m$ being the rate of transitions from $m$ to the neighboring spin levels. The overdamped condition $\Gamma_{m,m'} \gg \Delta$ is assumed, which is the case of practical interest. Since the $| m' \rangle$ state quickly decays down to the $| S \rangle$ state, the magnetization is given by

$$\sigma_z \equiv \langle S_z \rangle / S = 1 - 2n_{-S}.$$ 

(3)
At a constant sweep rate, $W = v_W t$, when $\Gamma_{m,m'}$ is small compared to the distance between adjacent spin levels, one can integrate Eq. (1) from $-\infty$ to $\infty$ to obtain the population of the $| - S \rangle$ state after the level crossing. This gives the Landau-Zener like asymptotic result,

$$n_{-S}(\infty) = e^{-\varepsilon},$$

with $\varepsilon$ corrected for thermally assisted tunneling [12],

$$\varepsilon = \frac{\pi \Delta_{mm'}^2 \exp \left( - \frac{E_m - E_{-S}}{k_B T} \right)}{2 \hbar v_W}.$$

The first magnetization step occurs when the tunnel splitting of the two states is sufficient to provide a not very small $\varepsilon$ for a given sweep rate $v_W$. All of the above formulas apply to the case of pure quantum tunneling that occurs at $T = 0$. In the latter case $m = -S$.

The above simple picture contradicts experiments. Indeed, according to Eq. (2) the width of the magnetization step due to the relaxation dynamics described by Eq. (1) is determined by $\Gamma_{m,m'}$. Such a width is very small compared to the experimental value. One could naively think that the relaxation of any individual molecule is still determined by Eqs. (1) and (2) but the resonant field is spread due to inhomogeneous dipolar and hyperfine fields, and due to structural disorder. This, however, cannot explain the height of the magnetization step as this would typically result in the total magnetization reversal during the first step. As we shall see, the non-trivial space-time dependence of the local energy bias $W$ due the evolution of the local dipolar field $B^{(D)}$ solves this controversy.

To simplify the problem we stick to the geometry of a long cylinder of length $L$ and radius $R \ll L$, and restrict our consideration by the longitudinal components of the fields. The transverse component of the field enters the problem through its known effect on $\Delta_{mm'}$. The bias at the cite $i$ is given by

$$W_i = (m' - m) g \mu_B \left( B - B_k + B^{(D)}_i \right) \equiv W_{\text{ext}} + W^{(D)}_i,$$

where $B_k$ is the resonant value of the external field for the $k$-th tunneling resonance ($k = S - m'$) in the absence of the dipolar field. The dipolar component of the bias is given by

$$W^{(D)}_i = \left( 1 - \frac{m'}{m} \right) E_{\text{D}} D_i, \quad D_i = \sum_j \phi_{ij} \sigma_j,$$

where $E_{\text{D}} \equiv (g \mu_B S)^2 / v_0$ is the dipolar energy, $E_{\text{D}} / k_B = 0.0671$ K for $\text{Mn}_{12}\text{-Ac}$, $v_0$ is the unit-cell volume, and

$$\phi_{ij} = \frac{3 (\mathbf{e} \cdot \mathbf{n}_{ij})^2 - 1}{r_{ij}^3}, \quad \mathbf{n}_{ij} = \frac{\mathbf{r}_{ij}}{r_{ij}},$$

is the dimensionless dipole-dipole interaction between the spins at the cites $i$ and $j \neq i$.

To write down the dynamical equation for the entire sample, it is convenient to use dimensionless variables

$$\tilde{t} \equiv \Gamma_{\text{res}} t, \quad \tilde{z} = \frac{z}{R}, \quad \tilde{W} \equiv \frac{W}{(1 - m'/m) E_{\text{D}}},$$

where

$$\Gamma_{\text{res}} = \frac{\Delta_{mm'}^2}{\hbar^2 E_{\text{D}}} e^{-(E_m - E_{-S})/(k_B T)},$$

is the relaxation rate on resonance, see Eq. (2). Equation (1) becomes a non-linear integro-differential equation,

$$\frac{d}{dt} n_{-S}(\tilde{z}, \tilde{t}) = -F(\tilde{z}, \tilde{t}) n_{-S}(\tilde{z}, \tilde{t}).$$

Here $F$ contains integral dependence on $n_{-S}(\tilde{z}, \tilde{t})$ via $\tilde{W}$,

$$F(\tilde{z}, \tilde{t}) = \frac{1}{1 + 4 E_{\text{D}}^2 W^2(\tilde{z}, \tilde{t})}, \quad \tilde{E}_{\text{D}} = \frac{(1 - m'/m) E_{\text{D}}}{\hbar \Gamma_{m,m'}}.$$

Summation of contributions from all sites in Eq. (1) gives the following expression for a continuous variable $W(\tilde{z}, \tilde{t})$:

$$\tilde{W} = \tilde{W}_{\text{ext}} + \tilde{W}^{(D)} = \tilde{W}_{\text{ext}} - \kappa [1 - 2 n_{-S}(\tilde{z}, \tilde{t})]$$

$$- 2 \pi \nu \int_{-L/(2R)}^{L/(2R)} d\tilde{z}' \frac{1 - 2 n_{-S}(\tilde{z}', \tilde{t})}{[(\tilde{z}' - \tilde{z})^2 + 1]^{3/2}},$$

where $\nu$ is the number of molecules per unit cell and

$$\kappa = \frac{8 \pi \nu}{3} - \sum_j \phi_{ij}.$$

The summation in the last formula goes over the volume of the wall of a large sphere. For the body-centered tetragonal lattice of $\text{Mn}_{12}\text{-Ac}$ one has $\nu = 2$ and $k = 14.6$ [13]. In
The metastable population behind the wall initiates by wall does not result in the total magnetization reversal.\[13\] Equations \((11)-(13)\) should be solved with the initial condition \(n_S(t = -\infty) = 1\).

For Mn_{12}-Ac \(\bar{E}_D\) is a large parameter, \(\bar{E}_D > 100\), so that one can naively think that \(F\) is always small except for a very brief period of time when the field sweep brings the bulk of the sample close to the resonance. If this was true, the total relaxation would have been vanishingly small. However, as we shall see below, the system finds the way to relax faster by forming a moving wall of finite width \(l \approx R\) inside which \(\bar{W}\) is so small that \(F\) is not significantly reduced from its maximal value \(F = 1\). Inside the wall region the resonant tunneling transitions take place. The greater is \(\bar{E}_D\), the closer to zero is the energy bias \(\bar{W}\) in the wall. Beyond the wall region \(\bar{W}\) deviates strongly from zero, \(F\) becomes very small, and the relaxation effectively freezes.

Numerical solution of Eq. \((11)\) based upon its discretization over the length of the sample yields a propagating wall of tunneling shown in Fig. 2. Spatial dependence of the metastable population \(n_{-S}\) and of the energy bias are shown in Fig. 3. Striking universal features of the relaxation process have been uncovered by the simulations. The wall ignites as the bias reaches the “magic” value of \(\bar{W}_{\text{ext}} = 4.3\), which corresponds to \(B = B_k + 194\text{G}\) in Mn_{12}-Ac regardless of the sweep rate and the level \(m\) that dominates the transition. One can see from Fig. 3 that everywhere in the wall the system is near the resonance, \(W \approx 0\). The reduced speed of the wall,

\[
v^* = \frac{v}{RT_{\text{res}}},
\]

depends on the parameter \(\bar{E}_D\). The propagation of the wall does not result in the total magnetization reversal. The metastable population behind the wall initiated by a slow sweep is a universal number \(n_f \approx 0.32\), see Fig. 4.

The width of the wall, \(2l\), is of the order of the diameter of the elongated sample. Figs. 2 and 3 show the tunneling wall and the quasiperiodic structure behind the wall in the left half of the sample. In a totally symmetric sample, two walls will simultaneously ignite on the left and on the right sides of the sample, and then move towards the center. Deviation from the dynamics depicted in the above figures will occur only when the distance between the two walls becomes comparable to \(R\). For \(L \gg R\) this should not change our conclusions.

So far we have not considered the effect of disorder on the formation of the tunneling wall. For Mn_{12}-Ac this question is important because nuclear spins, solvent disorder, and crystal defects produce randomness in the local values of \(B_k\) and local dipolar fields. To study the effect of disorder we added a random component, \(W_{\text{rand}}\), to the energy bias at each lattice site. While disorder produces visible fluctuations of \(n_{-S}\) and \(W\) behind the wall and ahead of the wall, the existence of the wall with \(W \approx 0\) is not affected by disorder, see Fig. 5.

We believe that our results are relevant to the magne-
magnetization steps commonly observed in molecular magnets at a slow field sweep. These results are robust with respect to other activation scenarios, e.g. those involving manifolds with a different total spin $S$ \cite{15}. The latter will simply modify the expression for $\Gamma_{\text{res}}$, Eq. (10).

Without dipolar fields the energy width of the magnetization step, according to Eq. (2), is $\Delta W = \hbar \Gamma_{\text{res}} / 2$. With account of the dipolar fields it is determined by $\Delta W = v_W t = v_W L/v = v_W L/(v^* \Gamma_{\text{res}})$. This gives the following ratio of the field widths of the magnetization step with and without the dipolar fields:

$$\frac{\Delta B}{\Delta B^*} = \frac{\pi}{v^* \varepsilon} \left( \frac{L}{R} \right),$$

(16)

where we have used Eqs. (3) and (14). For the parameters of Mn$_{12}$-Ac, in the limit of a very slow sweep, one numerically obtains $v^* \sim 10^{-3}$. At $\varepsilon = 30$ and $L/R = 30$ used in the simulations, Eq. (16) then gives $\Delta B / \Delta B^* \sim 10^3$. This brings the width of the step in the range that is usually observed in experiment. So far we have studied the dynamics of the first magnetization step. The second step begins with a quasiperiodic structure of magnetization left after the first step. This dynamics will be studied elsewhere based upon the equations derived above.

After this work was completed, it had come to our attention that the oscillating magnetization near tunneling resonance, depicted in Fig. 3, has been already seen in experiment \cite{16}. We encourage experimentalists to perform detailed local measurements of molecular magnets to confirm that the magnetization step involves propagating walls of quantum spin tunneling.

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