Time relaxation of interacting single-molecule magnets

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We study the relaxation of interacting single-molecule magnets in both spatially ordered and disordered systems. The tunneling window is assumed to be, as in Fe₈, much narrower than the dipolar field spread. We show that relaxation in disordered systems differs qualitatively from relaxation in fully occupied cubic and Fe₈ lattices. We also study how line shapes that develop in “hole-digging” experiments evolve with time t in these fully occupied lattices. We show (1) that the dipolar field h scales as p⁰ in these hole line shapes and (2) how p varies with lattice structure. Line shapes are not, in general, Lorentzian. More specifically, in the lower portion of the hole, they behave as (|h|/p⁰)(1/p−1) if h is outside the tunnel window. This is in agreement with experiment and with our own Monte Carlo results.

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1. INTRODUCTION

Magnetic relaxation in crystals of single-molecule magnets (SMM’s), such as Fe₈, has become a subject of great interest.¹–⁴ At low temperature T, each SMM behaves approximately as a single spin S. Magnetic relaxation at k_BT ≲ 0.1U/S, where U is a magnetocrystalline anisotropy barrier, is temperature independent, and is duly attributed to quantum tunneling under the barrier. Hyperfine interactions with nuclear spins as well as dipole-dipole interactions among all SMM electronic spins give rise to a variety of phenomena that are not yet fully understood. Hyperfine interactions enable spins to tunnel even when the ensuing Zeeman energy change 2ε_b is much larger than the tunnel splitting energy Δ, provided |ε_b| is smaller than some ε_w.⁵ For Fe₈, for instance, Δ ≈ 10⁻⁴ mK, ε_w ≈ 10 mK, and the rms value of the Zeeman energy δε_b is approximately 400 mK. We shall restrict ourselves to systems with ε_w ≪ δε_b. In these systems, the relaxation of the magnetization goes on long after time Γ⁻¹, where Γ is the spin relaxation rate for spins within the tunneling energy window (that is, spins for which |ε_b| < ε_w). Tunneling spins give rise to changing dipolar fields, which in turn bring new spins into the tunneling energy window, thus keeping a magnetic relaxation process from extinction. In this paper, we focus our attention on effects that stem from this process.

We consider here experiments of the sort that were reported by Wernsdorfer et al. in Ref. 6. In them, a crystalline sample of SMM’s is first quenched from k_BT ≈ 0.1U/S to k_BT = 0.1U/S in either (a) a weak applied magnetic field of a few millitesla, and later observed after the field is switched off at time t=0 or (b) a zero field, and later observed after a weak field is applied at t=0. We shall refer to the former as a field-cooled (FC) experiment and to the latter as a zero-field-cooled (ZFC) experiment. Both types of experiments can be lumped into one by defining $\tilde{m} = 1-m/m_0$, where $m_0$ is the initial magnetization in a FC experiment, and $\tilde{m} = m/m_s$, where $m_s$ is the final steady-state magnetization in a ZFC experiment. Wernsdorfer et al. observed that $\tilde{m} \propto \Gamma t^{1/2}$ over roughly two time decades. The time evolution of “holes” that, under suitable conditions, develop in the magnetization density function, have also been reported.⁶,⁷ The existing theory at the time⁵,⁸,⁹ predicted a universal $\sqrt{t}$ short time relaxation from a fully polarized system, but said little about relaxation from or into weakly polarized states.¹⁰ Other theories¹¹ take hyperfine interactions into account but disregard dipole-dipole interactions. They therefore apply if δε_b ≲ ε_w, which is not within the scope of this paper.

We have developed a theory¹²,¹⁴ that gives the time evolution both of $\tilde{m}$ and of the holes’ line shapes in weakly polarized systems of interacting SMMs, such as Fe₈, in which ε_w ≪ δε_b. There are three clearly discernible time regimes. For $\Gamma t \ll 1$, $\tilde{m} \propto \Gamma t$. In the second time stage, when $1 \ll \Gamma t$, up to some time before $\tilde{m} \sim 1$, $\tilde{m} \propto \sqrt{t}$, at least for all fully occupied cubic lattices. Moreover, the theory gives a simple relation that specifies how p varies with lattice structure. In FC experiments, $\tilde{m} \sim 1$ in the third time stage, that is, $m=0$. The third time stage is more interesting in ZFC experiments. Then $m(t)$ settles down temporarily to a quasistationary value $m_w$, which the theory predicts, if either k_BT ≫ ε_w or if the heat exchange rate with the lattice is much smaller than Γ; on the other hand, if k_BT ≫ ε_w is not satisfied and heat exchange rate with the lattice is not much smaller than Γ, then the relaxation of the magnetization shifts into a thermally driven approach to equilibrium, skipping the quasistationary state. A quite different treatment of relaxation from weakly polarized states that gives $1-m/m_0 \propto \sqrt{t}$, independently of the spins’ spatial distribution, is given by Tupitsyn, Stamp, and Prokof’ev (TSP) in Ref. 15, criticized in Ref. 13, and defended in Ref. 16. TSP’s treatment of relaxation from weakly polarized states is rather unrelated to the earlier theory² of Prokof’ev and Stamp for a $\sqrt{t}$ relaxation from fully polarized states, abut which we have nothing to say here. According to TSP, $\sqrt{t}$ relaxation in weakly polarized systems holds as long as $1 \ll \Gamma t$ and $\tilde{m} \ll 1$, that is, roughly, over the second time stage. This is also the time domain where our theory gives $\tilde{m} = (\epsilon_w/\delta\epsilon_b)(\Gamma t)^{1/2}$ for fully occupied lattices. This time stage, sometimes referred to as “short times,” can in fact be arbitrarily large, for arbitrarily small $\epsilon_w$, since $\tilde{m} \ll 1$ only implies $\Gamma t \ll (\delta\epsilon_b/\epsilon_w)^{1/2}$. Note also that
Thus providing another test for our theory. Other spatial distributions, namely, under full spatial disorder, the number densities of up and down spins, respectively, with a lattice types... from our theory the time evolution of $f(h,t)$, follows immediately. As we have shown recently, the above scaling form holds approximately for sc and Fe$_8$ lattices (as defined in Ref. 18), but not in general. It fails, for example, for fcc, bcc, and diamond lattices. Our theory also gives the time evolution of $f(h,t)$, but follows from a more fundamental assumption: that the dipolar field on any one given site changes by some random amount $\Delta h$, whenever a spin flips somewhere else for the first time, and that $\Delta h$ follows a Lorentzian distribution (for more details see Secs. II A and III A, and Ref. 14). The integro-differential equations for the evolution of $f(h,t)$ and of the magnetization that obtain in our theory follow from this assumption.

Unfortunately, as far as we know, only experiments on a crystalline Fe$_8$ structure have thus far been performed. However, MC simulations have been performed for various fully occupied cubic lattices, which have given values of $p$ that agree with our predictions. This paper’s first aim is to extract from our theory how the magnetization is supposed to relax in Fe$_8$, compare this with experiment over the time span where published experimental data exist, and make predictions for later times. It is also our purpose to predict, and check with MC simulations, how $m$ relaxes with $t$ for other spatial distributions, namely, under full spatial disorder, thus providing another test for our theory.

The holes observed in the experiments described above are also of interest. They correspond to “wells” that develop in the function $f(h,t)=p_1(h,t)-p_2(h,t)$ (defined above). From the relation $m(t)=-\int dh f(h,t)$, the time evolution of $m$ follows, but $f(h,t)$ provides additional information about the magnetic evolution of the system that $m(t)$ does not. For short times, that is, for $t/\Gamma \ll 1$, the hole’s width is equal to $\epsilon_w$. This was first surmised by Wernsdorfer et al. to propose a number, approximately 10 mK, for the tunneling energy window $\epsilon_w$. However, we know of no published data for the hole line shape evolution well into the intermediate time range, that is, for $1 \ll t/\Gamma$. Our second aim is to fill this gap. To this end, we work out from our theory the time evolution of the hole line shapes in this time stage in fully occupied cubic systems and Fe$_8$ crystals, and check the results obtained against our MC results. We also obtain results of a more general nature for the hole line shape. Before we state our results, we specify the model.

### Table I. Quantities $h_0$, $\sigma$, and $\sqrt{\langle h^2 \rangle_0}$ are given for randomly oriented spins on the lattices specified. $h_0=\bar{n} \pi \sigma^2/3^{5/2}$, $\sigma=\{2 \pi p_0(0)\}^{-1}$, where $p(0)$ stands for the probability distribution function at $h=0$, and $\langle h^2 \rangle_0$ is the rms spatial average of the dipolar field. For all lattices except for Fe$_8$, $h_0$, $\sigma$, and $\sqrt{\langle h^2 \rangle_0}$ are given in terms of $h_d$. All lattices are fully occupied, except for the “dilute sc,” which stands for a sc lattice with $\bar{n} \ll 1$ sites occupied. Finally, $\alpha=8 \pi^2/3^{5/2}$.

<table>
<thead>
<tr>
<th>Lattice</th>
<th>$h_0$</th>
<th>$\sqrt{\langle h^2 \rangle_0}$</th>
<th>$\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>sc</td>
<td>$\alpha$</td>
<td>3.655</td>
<td>3.83(2)</td>
</tr>
<tr>
<td>bcc</td>
<td>$2 \alpha$</td>
<td>3.864</td>
<td>4.03(2)</td>
</tr>
<tr>
<td>fcc</td>
<td>$4 \alpha$</td>
<td>8.303</td>
<td>8.44(2)</td>
</tr>
<tr>
<td>Fe$_8$</td>
<td>47(1) mT</td>
<td>46(1) mT</td>
<td>31(1) mT</td>
</tr>
<tr>
<td>Dilute</td>
<td>$\alpha \bar{n}$</td>
<td>$\sqrt{\pi/2}h_0$</td>
<td></td>
</tr>
</tbody>
</table>

We assume an easy anisotropy axis as given in Refs. 23, 24, and 28.

### A. The model

All spins are on a lattice, they point along the easy anisotropy axis, and interact as magnetic dipoles. We consider both fully and partially occupied lattices. Let the magnetic field at site $i$ produced by spin $S_j$ at site $j$ be given, in the usual notation, by $h_{ij}=h_j(a/r_{ij})^3[1-3(z_j/r_{ij})^2]$, where $r_{ij}$ is the distance between the $i$ and $j$ sites, $a$ is the distance between nearest neighbor sites, $h_j=(\mu_0/\sqrt{8 \pi})g_\mu_S S_j S_j$, and $S_j=\pm S$ for all $i$. Furthermore, let the magnetic field $h_j$ at site $i$ be given by $h_{ij}=S_j h_{ij}$, where $S_j$ is over all occupied lattice sites. The tunnel window size and tunneling rate $\Gamma$ are defined next. At very low temperature, that is, if $k_B T \leq 0.1 U/\Sigma$, a spin can flip only if the field $h_j$ acting on it satisfies $|h_j|<h_{w2}$. The flipping rate is $\Gamma$ if upon tunneling the energy decreases, but if the energy increases by $\Delta E$, then the rate is $\Gamma \exp(-\Delta E/k_B T)$, following detailed balance. [Even though $|\Delta E|<\epsilon_w$ and usually $k_B T \gg \epsilon_w$, $\exp(-\Delta E/k_B T)$ is not quite equal to 1, and this makes a difference after a sufficiently long time, as is shown below.] We also simulate relaxation processes in which the energy $E$ is assumed to remain constant (such as if no spin-lattice relaxation takes place). Then, we assume a value of $T$ is such that $E$ remains approximately constant. No tunneling window restriction applies for spin flips if $k_B T \approx U/\Sigma$.

We let $p(h,t)$ be the probability density function (PDF) that any one given spin have field $h$ at time $t$, let $p_0(h)$ be the same distribution for a completely random spin configuration, and let

$$\sigma=\{2 \pi p_0(0)\}^{-1}.$$  (1)

For a Gaussian field distribution, $\sigma$ is equal to the dipole field rms value $\langle h \rangle$ for a random spin configuration (see Table I), but this is not so in general. Values of $\sigma$ that follow from MC simulations for cubic and Fe$_8$ lattices with randomly oriented spins are given in Table I. Finally, let $h_0=(8 \pi^2/3^{5/2})\bar{n} \pi$, where $\bar{n}$ is the number of dipoles per unit cubic cell. Randomly oriented spins on a cubic lattice give a Lorentzian field distribution of $h_0$ half width at half maxi-
Section II is devoted to the relaxation of the magnetization. The equations from our theory\textsuperscript{14} which we use to calculate the time evolution of the magnetization are restated in Sec. II A. The results that follow from them for Fe\textsubscript{8} crystals are shown to agree rather well with experiment and with our own MC results in Sec. II B. The evolution we predict for $m(t)$ as well as our MC results cover a time span that is two orders of magnitude longer than the experimental one $\tau_E (\tau_E \approx 20 \text{ min})$. Let $\tau_n$ be the end time for the regime where $m \approx \varphi$. We showed in Ref. 14 that $\tau_n = \Gamma^{-1}(\sigma/h_0)^{1/p}$ from which we obtain $\tau_n \approx 10 \tau_E$. For $\tau_n \approx \tau$, the evolution of $m(t)$ is shown to depend sensitively on $T$ if good thermal contact with a heat reservoir is assumed. If on the other hand we assume constant energy processes (i.e., no spin-lattice relaxation), then $m$ levels off, if only temporarily, to a stationary value $m_s$ when $\tau_n \approx \tau$. The value of $m_s$ we obtain from theory is unrelated to the equilibrium value of $m$, which only obtains much later. This stage, when $m \approx m_s$, sets in after most spins in the system have tunneled at least once after the magnetic field is applied. Simulations bear this out. We also obtain, from theory as well as from MC simulations, $m(t)$ for spatially disordered systems. More specifically, we make a random selection of a fraction $\bar{n}$ of $L \times L \times L$ sc lattice sites and place spins on them. For $\bar{n} \approx 0.1$, we assume full disorder. Then, theory predicts a magnetic relaxation that bears no resemblance to a $\varphi t$ rule, not even to the $\varphi^2 t$ rule that we refer to as the “annealing energy,” is $-\Delta m / \Gamma$. Any attempt to decode in a compact form immediately below, give the magnetization $m(t)$ at time $t$, and $n(t)$, the fractional number of spins that flip at least once in time $t$. We first recall an important ingredient of the theory for ZFC experiments:\textsuperscript{14} the energy per spin at the time when the system is quenched, which we refer to as the “annealing energy,” is $-\Delta m / \Gamma$. Let $x_1 = m g \mu_B S \sigma (h)^2 / (\varepsilon_s h_0 H)$ and $x_2 = 2(\sigma/h_0)(1-m/m_0)$, for ZFC and FC experiments (defined in the Introduction, respectively, and $x_2 = n \sigma/h_0$ for both FC and ZFC experiments. The desired equation follows,

$$
\frac{dx_j}{dt} = a_j \sqrt{\frac{2}{\pi}} - b_j \int_0^\infty \frac{dx_j(\bar{\tau})}{d\bar{\tau}} \frac{1}{\omega(t - \bar{\tau}) + 1},
$$

where
When \( h_\omega \) flip. Since \( m(t) \) returns to its initial state, thus canceling the effect of the first flip. When a spin flips a second time, it only matters whether fully occupied or not. It follows that leveling off of \( m(t) \) has to do with the fact that a spin flip contributes to hole evolution, when \( h_\omega \) is switched on. When a spin flips a second time, it only matters whether fully occupied or not. It follows that leveling off of \( m(t) \) has to do with the fact that a spin flip contributes to hole evolution, when \( h_\omega \) is switched on.

We have shown analytically in Ref. 14 that \( m \approx x^p \) and \( n \approx x^p \) satisfy Eq. (6) for \( j = 1 \) and in the \( 1 \leq \Gamma t \leq (\sigma/h_\omega)^{1/p} \) time range if \( p \) is given by Eq. (5). Numerical solutions of Eq. (6) show that \( m \approx x^p \) ensues in the wider range \( 1 \leq \Gamma t \leq (\sigma/h_\omega)^{1/p} \) time span for fully occupied cubic lattices. \(^{14}\) We show below that this is also so for a fully occupied Fe lattice.

Spatially disordered systems behave differently. Consider a very small fraction \((\tilde{n} \ll 1)\) of sites of a sc lattice to be occupied by randomly oriented spins. Then, a Lorentzian dipolar magnetic field distribution \(^{26}\) of half-width \( h_\sigma \) ensues. It follows then, from the definition of \( \sigma \) and of \( h_\omega \), that \( \sigma/h_\omega = \sqrt{\pi}/2 \). The number \( p = 0 \) follows then from Eq. (5). Recall, however, that theory implies that this ensues only when \( \Gamma t \gg 1 \). For earlier times, more specifically, for all \( \Gamma t \approx 1 \), we find that the numerical solution from Eq. (6) is well fitted by Eq. (2) if \( \tilde{n} \leq 0.1 \). Numerical solutions of Eq. (6) are plotted in Fig. 2(a) for \( \tilde{n} = 1 \) and 0.6, both for \( h_\omega = 0.02 \) and in Fig. 2(b) for (1) \( \tilde{n} = 0.1 \) and \( h_\omega = 0.02 \), and (2) \( \tilde{n} = 0.03 \) and \( h_\omega = 0.006 \). Note that the same solution obtains for the latter two cases. We come back to these figures in Sec. II B.

### B. Comparison with experiments and simulations

We first make use of Eqs. (6) and (7) to obtain \( m(t) \) for Fe. Some numbers must first be fed into Eqs. (6) and (7). For \( h_\omega \), we use \(^{27}\) 0.8 mT, as given in Ref. 6. We use \( \Gamma = 0.04 \) s\(^{-1}\) (see Refs. 14 and 21). With the numbers given in Table I for \( \sigma \) and \( h_\sigma \), we obtain \( x_1(t) \) and \( x_2(t) \) numerically from Eqs. (6) and (7). Finally, the value of \( -\epsilon_\omega \), the annealing energy, \(^{14}\) is needed in order to obtain \( m \) from \( x_1 \). Not knowing \( \epsilon_\omega \), we treat it as a fitting parameter. We find \( \epsilon_\omega \approx 36 \) mK fits best the experimental data points from Ref. 6, which are shown in Fig. 3 for a few applied fields. The energy \( \approx 36 \) mK may be compared to the approximate value \( \approx 500 \) mK of the ground-state energy. \(^{28}\)

The MC data points shown in Fig. 3 follow from simulations in which the system first evolves at some high temperature (a few kelvin) for a short time (less than 1 MC sweep) until the energy equals \( \approx 36 \) mK. At such temperatures, Fe cluster spins are not forced to tunnel through the ground-state doublet. Accordingly, all spins are allowed to flip, regardless of the dipolar field acting on them. We explore different scenarios after quenching. In our theory, we assume no energy exchange takes place between the spin system and a heat reservoir. We have also performed MC simulations under this assumption. This is approximately realized for the time range exhibited in Fig. 3 by flipping only spins within the tunnel window, and then with equal probabilities for upward or downward flips. If, on the other hand, heat exchange does take place readily, as one gathers from Ref. 29, where

\[
\omega(t') = \min \left( \frac{\pi h_\omega}{2\sigma} x_2(t'), \sqrt{\frac{\pi \sigma}{2 h_\omega}} x_2(t') \right),
\]

\( a_1 = 4, b_1 = 2 \). In order to obtain \( x_1, \) Eq. (6) must first be solved for \( j = 2 \), letting \( a_2 = 1 \) and \( b_2 = 1 \), in order to then use \( x_2(t') \) in Eq. (7), and thus enable substitution of \( \omega \) into Eq. (6) for \( j = 1 \).

The theory applies if \( h_\omega \ll \sigma \) and the energy is constant, that is, if no energy transfer to the phonon bath takes place. This is also approximately so if \( kT \gg \epsilon_\omega \). If the constant energy condition is not met in a ZFC experiment, a linear in time magnetization relaxation that is thermally driven takes over before \( m(t) \rightarrow m_{eq} \). The theory also gives

\[
m_{eq} = 2He_\omega/\mu g S \mu_B (\hbar^2/4).\]

Note that the definition of \( x_1(t) \), together with Eqs. (6)–(8) imply that the time variation of \( m(t)/m_{eq} \) in a ZFC experiment is the same as \( 1 - m/m_{eq} \) in a FC experiment.

A few remarks about Eqs. (6) and (7) are in order. Clearly, \( x_1(t) \) only depends on two parameters: \( h_\omega \) and \( \sigma \). The latter only comes into play at the later portion of the time evolution, when \( n(t) > 2\sigma^2/(\pi h_\omega) \), which is when \( m(t) \) starts leveling off. Now, \( 0.4 \leq \sigma/h_\omega \leq \sqrt{\pi}/2 \) for all cubic lattices, whether fully occupied or not. It follows that leveling off of \( m(t) \) is triggered some time (see below) while \( n(t) \approx 1 \). This has to do with the fact that a spin flip contributes to hole widening in \( f(h,t) \) the first time it takes place after the field is switched on. When a spin flips a second time, it only returns to its initial state, thus canceling the effect of the first flip. Since \( m \) is proportional to the width of the hole in \( f(h,t) \) when \( \Gamma t \approx 1 \) it follows that \( m(t) \) becomes constant when \( n \approx 1 \). The time when \( m(t) \) levels off is illustrated in Fig. 1, for fully occupied fcc lattices. For instance, for \( h_\omega = 0.01 \), theory predicts \( m(t) \) to start leveling off when \( n(t) \approx 0.11 \) since \( 2\sigma^2/(\pi h_\omega) = 0.11 \). Thus, a significant portion of the evolution, up to \( n \approx 1 \), only depends on \( h_\omega \). Information about the lattice or degree of spatial disorder only comes into the equations through this number. Other numbers, such as \( h_{\omega}, e_\sigma \), and \( H \) only come into the proportionality factor between \( x_1 \) and either \( m \) or \( 1 - m/m_{eq} \). The temperature does not enter anywhere into the equations.
heat exchange rates that are comparable to $\Gamma$ are found, then
detailed balance should be enforced in MC simulations. The
results of doing this lead to the plots shown in Fig. 3 for $T$
= 40 and 300 mK.

Results obtained from theory, in Sec. II A for very disor-
dered systems are shown in Fig. 2(b) for $\bar{n}=0.1$ and $h_w$
=0.02 and for $\bar{n}=0.03$ and $h_w=0.006$. Monte Carlo data
points are also shown for the same values of $\bar{n}$ and of $h_w$.
Data points for $\bar{n}=0.1$ and $h_w=0.02$ fall on top of data points
for $\bar{n}=0.03$ and $h_w=0.006$. This is as expected, since $\sigma/\bar{n}$,
for full spatial disorder, implies that $\sigma/h_w$ has the same value
in both cases and theory predicts independence from any
other parameter. The fitting function from Eq. (2) falls right
on top of the curve for theory in Fig. 2(b), and cannot there-
fore be shown separately.

Finally, we consider size effects. For a $16 \times 16$ lattice and $\bar{n}=0.1$, for instance, approximately 410 spins make up
the system. Of these, only approximately a fraction $2p(0)h_w$
are within the tunnel window. That is, approximately
820$h_w/\pi h_0$ spins, which only amounts to some 12 spins, are
within the tunnel window. For this reason, we also simulated
$32 \times 32 \times 32$ and $64 \times 64 \times 64$ lattices for $\bar{n}=0.1$ and 0.03,
respectively. Monte Carlo data points are shown in Fig. 2.
Clearly, no significant size effects are observed.

FIG. 2. (Color online) (a) Magnetization versus $\Gamma t$. Lines are for
theory and symbols are for data from MC simulations of $L \times L$
sc lattices with a fraction $\bar{n}$ of their sites occupied. For $\bar{n}=0.6$
the dashed line is for theory, $\Diamond$ and $\heart$ are for MC data for $L=32$
and 16, respectively. For $\bar{n}=1$ the full line is for theory, $\triangle$ and $\blacksquare$
are for MC data for $L=32$ and 16, respectively. All symbols are
from averages of 800 MC runs while $L=32$ and 16, respectively. For $\bar{n}=1$ the full line is for theory, $\triangle$ and $\blacksquare$
are for MC data for $L=32$ and 16, respectively. All symbols are
from averages of 800 MC runs while $\Gamma t>10^3$. (b) Same as in (a) but for $\bar{n}=0.1$ and $h_w=0.02$, and for $\bar{n}=0.03$ and $h_w=0.006$. The full line is for theory for both values of $\bar{n}$.
For $\bar{n}=0.03$, $\Diamond$ and $\heart$ stand for MC data for $L=64$ and 32,
respectively. For $\bar{n}=0.1$, $\blacktriangleleft$ and $\blacktriangledown$ stand for MC data for $L=32$ and 16, respectively. As in (a), all symbols are from averages of 800 MC runs while $\Gamma t<10^3$ and 40 MC runs when $\Gamma t>10^3$.

FIG. 3. (Color online) Magnetization versus time in hours. Units
for $m$ are such that $m=1$ for full polarization. $\Diamond$, $\square$, and $\bigcirc$ are for experimental data taken from Ref. 6 for $H=3.92$, 2.24, and
1.12 mT, respectively. Full lines are from our MC simulations for
$kT\approx kT_{\text{ex}}$, and dashed lines are for theoretical predictions, that is,
from Eqs. (6) and (7). Data points that follow from MC simulations
for $H=3.92$ mT are also shown for $T=40$ ($\blacksquare$) and 300 mK ($\triangle$). We
assumed (Refs. 6, 14, and 21) $h_0=0.8$ mT and used the values of $\sigma$
and $h_0$ that are given in Table I. In the simulations, the initial state
was prepared at $T=2$ K. At this temperature we allowed the simu-
lation to proceed in time up to the point when the energy of the
system reached $-36$ mK, which is 0.07 of the ground-state energy.
This is the value of $x_0$ we used in order to relate $x_1$ and $m$, just
above Eq. (6). We treat one MC sweep as $\Gamma t=1$ and assume (Ref.
14) $\Gamma t=0.04$ s$^{-1}$ in order to convert MC sweeps to hours. Note
that $x_0=3$ h, since $\sigma=31$ mT and $h_0=0.8$ mT.

III. TIME EVOLUTION OF THE LINE SHAPE

In this section we first derive some results for $f(h,t)$ that
are valid whenever $m \propto \rho^p$ holds. We know from Ref. 14 and
from the previous section that $m \propto \rho^p$ holds in the time span
$1 \leq \Gamma t \leq (\sigma/h_0)^{1/p}$ for fully occupied sc, fcc, bcc, and Fe$_8$
lattices, but we now know it is not so for spatially random
systems. The results we derive below are applied to fully
occupied Fe$_8$ and fcc lattices and are compared to results
from experiment (for Fe$_8$) and from MC simulations.

A. Theory

The starting points for the derivation are the following
two equations, from Ref. 14:

$$g(h,t) \approx \int_0^t d\tau \frac{dn(\tau)}{d\tau} G(h + H, t - \tau)$$

(9)

and

$$G(h, H, t - \tau) = \frac{u(t - \tau)}{\pi[(h + H)^2 + u(t - \tau)^2]},$$

(10)

where $g(h,t)=f(h,0)-f(h,t)$, $u(t)=h_0\rho(t-\tau)$, and
$n(t-\tau)$ is the fractional number of spins that flip at least once
in time $t-\tau$. The rationale for these two equations is given
next, but [if $|h+H| \ll \sigma$ and $\Gamma t \approx (\sigma/h_0)^{1/p}$] Eqs. (9) and (10)
also follow from Eqs. (13) and (14) of Ref. 14, respectively.
Assume that, between times \( t \) and \( \tau \), a fraction \( n(t - \tau) \) of all spins flip at least once and that \( n(t - \tau) \ll 1 \). This can later be checked to be satisfied if \( t \ll \tau_w \), where \( \tau_w = \Gamma^{-1}(\sigma/h_w)^{1/p} \).

Then, Eq. (10) gives the probability density \( G(h, H, t - \tau) \) that, at time \( t \), the field is \( h + H \) at a site where the field at time \( \tau \) was 0.26. To understand Eq. (9), note first that the definition of \( g(h, t) \) implies that \( g(h, t) \) must satisfy \( f dhg(h, t) = m(t) - m(0) \). Equation (9) does give \( m(t) - m(0) = \int d\omega \mu d\tau d\sigma \), since \( f dhG(h, H, t - \tau) = 1 \). Similarly, a variation in the magnetization \( (dm/d\sigma)d\tau \) coming from some spin flipping between times \( \tau \) and \( \tau + d\tau \), when the field \( h + H \) acting on them was within the tunnel window, contributes to \( g(h, t) \) with a Lorentzian curve whose width is \( h_h \rho(t - \tau) \), where \( n(t - \tau)/2 \) is approximately the fraction of the total number of sites where spins at time \( t \) point opposite to the way they did at time \( \tau \). Furthermore, the area under the Lorentzian must be given by \( (dm/d\sigma)d\tau \). That explains Eq. (9).

We make use of \( n(t - \tau) = \tilde{m}(t - \tau) \),14 and of

\[
\tilde{m}(\tau) = 1.1 \frac{h_h}{\sigma} \Gamma(\tau)^p, \tag{11}
\]

which has been shown to hold for all fully occupied cubic and \( \text{Fe}_8 \) lattices in Ref. 14 and in Sec. II B, respectively, while \( 1 \leq \Gamma(\tau)^p \ll \sigma/h_w \). We then divide by \( f(h, 0) \), which, for \( h \ll \sigma \) is approximately given by \( m_0/\sqrt{2\pi}\sigma \).14 Finally, the change of variable \( x = \tau/H \) brings, if \( 1 \ll \Gamma(\tau)^p \ll \sigma/h_w \) and \( h_w \ll |h + H| \ll \sigma \), to which Eq. (9) into

\[
\frac{f(h, t)}{f(h, 0)} \approx 1 - \frac{\sin \pi p}{\pi} \int_0^1 dx \frac{e^{-x^p}}{(\alpha \tilde{\eta}^2 + (1-x)^2)^p}, \tag{12}
\]

where \( \alpha \approx 0.8(\sigma/h_0)^2 \). Both Eqs. (3) and (12) show that the field \( h \) scales as \( \rho^p \) in the hole line shapes.

Finally, to obtain Eq. (3) from Eq. (12), note first that \( f(0, t)/f(0, 0) \to 0 \) as \( t \to \infty \) in Eq. (12), since the integral therein equals \( \pi/sin \rho \pi \) if \( \pi = 0 \).30 Then, breaking up the integration interval into two pieces, (1) from 0 to \( (\alpha \tilde{\eta})^{1/2p} \), and (2) from \( (\alpha \tilde{\eta})^{1/2p} \) to 1, and expanding \( \chi^p/(\alpha \tilde{\eta}^2 + (1-x)^2)^p \) in powers of \( \epsilon \) and \( 1/e \) in the first and second integration intervals, respectively, where \( \epsilon \approx \chi^p/\alpha \tilde{\eta}^2 \), gives \( |\tilde{\eta}|^{1-p} \) for the leading term, which is the desired result, that is, Eq. (3).

### B. Comparison with experiments and simulations

In this section we test our results, that is, the validity of Eqs. (3) and (12), against experiments6 and against our MC simulations.

We first apply Eqs. (3) and (12) to \( \text{Fe}_8 \). From Table I, \( \sigma/h_0 = 0.66 \) follows. Substitution of this number into Eq. (5) gives \( p = 0.58 \). Knowing the value of \( p \) we can plot the data points for \( \text{Fe}_8 \) shown in Fig. 4(a).

Unfortunately, data for holes in \( \text{Fe}_8 \) have only been published for \( t \ll 40 \), so that, is, for \( \Gamma \ll 1.6 \), a time which falls short of the validity range for Eqs. (3) and (12). Still, one can appreciate in Fig. 4(a) how the data points seem to approach the theory curve for \( f(h, t)/f(h, 0) \) as \( t \) increases up to \( \Gamma \ll 1.6 \).

In order to see how this would go for longer times, we have used our model to simulate an experiment on \( \text{Fe}_8 \). The results are shown in Fig. 4(b). We have let one MC sweep equal \( \Gamma = 1 \), which, by the argument given above, implies \( t = 25 \) s for \( \text{Fe}_8 \). The agreement with theory is remarkable. This is better appreciated in the log-log plot shown, with the same data, in Figs. 5(a) and 5(b). On the other hand, rescaling these plots, using \( p = 1/2 \) gives rise to some data point scatter, but not sufficiently large to convincingly rule out \( p = 1/2 \). This is not too surprising, given the small difference between \( p = 1/2 \) and the value \( p = 0.58 \) that is given by Eq. (5).

Still, one might have hoped that these data would have been sufficient to discriminate between Eq. (3), where \( \eta \) is raised to the \( 1/p-1 \) power and the Lorentzian curve of Ref. 15. Again, data for smaller values of \( \eta \) would be required for this. We know of no other experimental results for hole digging we can make use of. As far as we know, all other reported experiments for SMM systems start from strongly polarized initial states.20

Consequently, we decided to do simulations of SMM’s in fcc lattices, because Eq. (5) gives then a value 0.73 for \( p \), which differs significantly from 1/2. We are now at liberty to choose the value of \( h_w \). In order to be able to obtain hole line shapes down to rather small values of \( \eta \), and still meet the validity criterion for Eqs. (3) and (12), we let \( h_w \) take values down to 0.01.

We show how \( m \) varies with \( t \) in Fig. 1 in a simulated experiment in which all spins are up and down with prob-
Figure 5. (Color online) (a) Everything is as in Fig. 4(a), except that a log-log scale is used here. (b) Same as in (a) but for MC simulations. Everything else is as in Fig. 4(b). The dashed line stands for $x^{1/2}$, as predicted by Eq. (3) for $p=0.58$, for Fe$_8$.

Figure 6. (Color online) (a) $f(h,t)/f(h,0)$ versus $\eta$, defined in Eq. (4), for the shown times. Times are in MC sweeps. $h_w=0.01$. Symbols stand for averages over 1400 MC runs for 65 536 spins in a fcc lattice. The full line is from Eq. (12). As in Fig. 4, initially, all 65 536 spins are randomly up or down with probabilities 0.6 and 0.4, respectively. (b) Same as in (a) but in a log-log scale. The solid line stands for Eq. (12) and the dashed line is for the best-fitting Lorentzian curve. The dash-dotted line stands for $\eta^{1/0}$, as predicted by Eq. (3), for $p=0.73$, given by Eq. (5) for fcc lattices.

Figure 7. Hole line shapes obtained from MC simulations are shown in Figs. 6(a) and 6(b). The nice agreement with theory is reassuring. Similar plots but using $p=0.5$ give unsatisfactorily wide data point scatter. The data clearly follow Eq. (3) for $\eta\ll 1$ and deviate sharply from a Lorentzian line shape. We do not exhibit results for sc or bcc lattices, but we have found them to follow our predictions equally well.

IV. CONCLUSIONS

Results that follow from our theory for the relaxation of the magnetization of interacting SMM's are reported. They are in fair agreement with the experimental relaxation of the magnetization observed in Fe$_8$ as well as with our own MC results for Fe$_8$ and for other lattices. Furthermore, we make some predictions for Fe$_8$ that can be checked experimentally. Experiments following the lead of Ref. 6 would be made feasible by the application of a transverse field $H_z$ of approximately 0.3 T, since $\Gamma$, which increases as $\Delta^2$, would then increase by a factor of roughly 50 if $H_z$ is applied along the easier magnetization direction on the $xy$ plane (see Figs. 2 and 3 of Ref. 4). This would in effect approximately reduce the time scale in Fig. 3 from hours to minutes. Comparison of experimental results with MC data shown in Fig. 3 would be interesting. It would, for instance, show whether heat exchange takes place readily, as inferred in Ref. 29 from nuclear magnetic resonance experiments, or not.

We have also shown, from theory and MC simulations, that the magnetization of spatially disordered SMM's relaxes, not as any power of time, but approximately as given by Eq. (2). A counterintuitive prediction that follows from our theory and from MC simulations can be gathered from Figs. 2(a) and 2(b). One might have thought that dilution would lead to weaker dipole interactions and, consequently, to unhindered, faster relaxation. Instead, the opposite effect takes place for $0.1 \lesssim \bar{n} \lesssim 1$ after some time.

Line shapes that develop in crystals of Fe$_8$ clusters have been obtained from our theory. We have shown that $f(h,t)$ is only a function of $h/t\rho$ for all $|h| > h_w$, that is, for all $h$ outside the tunnel window. This is the main content of Eq. (12). Furthermore, we have shown that data points from experiments on Fe$_8$, taken from Ref. 6, as well as results from MC simulations we have performed for the same system, follow this rule. Scaling also ensues for the data from our MC simulations of SMM's on fcc lattices for $p=0.73$, as given by Eq. (5), but not for the otherwise predicted $p=1/2$ value that is supposed to hold universally.

We have also shown that $f(h,t) \sim |h/t\rho|^{1/2}$ if $h_w/\sigma \ll \eta \ll 1$ and $h$ is outside the tunnel window. Again, this is in agreement with experimental and MC results for Fe$_8$. [see
Figs. 5(a) and 5(b)], fcc [see Figs. 6(a) and 6(b)], and (not shown) sc and bcc lattices. A rough argument that explains why holes line shapes are not Lorentzian follows. Note first that while field distributions from dilute systems of dipoles are indeed Lorentzian,\(^\text{20}\) only spin flips that take place after time \(t\) contribute to the diffusion of a hole that was “dug” at time \(t\). Since a full hole is only dug gradually in the course of time, a sum of Lorentzian functions of \(h\) [see Eq. (12)] of various widths is expected. Not surprisingly, a Lorentzian function does not ensue for \(f(h,t)\) [see, Eq. (3)]. Here, experimental data for holes in the hundreds of seconds time range, over which the magnetization has already been observed experimentally, would be helpful.

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\(^{10}\)Except perhaps for an erroneous statement that is made in Ref. 5, to the effect that relaxation from weakly polarized states proceeds exponentially.


\(^{19}\)MC results for fcc lattices that are in sharp disagreement with the scaling rule \(f(h,t)=f(h/t^2)\), which TSP hold to be lattice independent, are exhibited in Ref. 13.

\(^{20}\)A justification of this model for the magnetic relaxation of single-molecule magnets on a crystal at low temperatures has been given by J. F. Fernández, Phys. Rev. B \textbf{66}, 064423 (2002).


\(^{22}\)More generally, for noncubic lattices, \(h_0=(8\pi^2/3^{5/2})\mu_B\rho_0\), where \(\rho_0\) is the dipole number density.


\(^{24}\)Whether \(h_0=0.8\) mT as it appears in Ref. 6, or \(h_0=0.4\) mT for “standard” Fe\(_{8}\), as it appears in Ref. 7, is not too important for our purposes. If \(h_0=0.4\), then \(e_{\alpha}=72\) mT, instead of \(e_{\alpha}=-36\) mT, would have to be assumed, since only the product \(h_0e_{\alpha}\) enters into the theory.

