Magnetization Process of Single Molecule Magnets at Low Temperatures

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We show that correlations established before quenching to very low temperatures later drive the magnetization process of systems of single molecule magnets, after a magnetic field is applied at $t = 0$. We also show that in simple cubic lattices $m \propto \sqrt{t}$, as observed in Fe_8, but only for $1 + 2\log_{10}(h_d/h_w)$ time decades, where h_d is a nearest neighbor dipolar magnetic field and a spin reversal can occur only if the field on it is within $(-h_w, h_w)$. However, the $\sqrt{t}$ behavior is not universal. For bcc and fcc lattices, $m \propto t^p$, but $p \simeq 0.7$. The value to which m finally levels off is also given.

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Magnetic clusters, such as Fe_8 and Mn_{12}, that make up the core of large organometallic molecules behave at low temperatures as large single spins. Accordingly, these molecules have come to be known as single molecule magnets (SMM's) [1]. In crystals, magnetic anisotropy energies U inhibit magnetic relaxation of SMM's, which can consequently take place at very small temperatures only through magnetic quantum tunneling (MQT). Dipolar interactions play then an essential role. They can give rise, upon tunneling, to Zeeman energy changes of nearly 1 K. This exceeds by many orders of magnitude the ground state tunnel splitting energy Δ that would follow from perturbations by higher anisotropies for Fe_8 and Mn_{12} [2]. Energy conservation would make MQT, which has been observed experimentally [3], impossible for the vast majority of spins in the system. Hyperfine interactions between the tunneling electronic spins of interest and nuclear spins open up a fairly large tunneling window of energy ε_w such that tunneling can occur if the Zeeman energy change $2\varepsilon_h$ upon tunneling is not much larger than ε_w [4]. More precisely, the tunneling rate Γ' for spins at very low temperature is given by

$$\Gamma'(\varepsilon_h) \simeq \Gamma \eta(\varepsilon_h/\varepsilon_w), \tag{1}$$

where Γ is some rate (whose value is not important for our purposes), $\eta(x) \sim 1$ for $|x| < 1$, $\eta(x) \sim 0$ for $x > 1$, and $\varepsilon_w \gg \Delta$. Other theories for MQT of SMM at very low temperatures have also been proposed [5]. We adopt Eq. (1) here, regardless of theory or physical mechanism behind it. We let $\eta(x) = 1$ for $|x| < 1$ and $\eta(x) = 0$ for $x \geq 1$ and refer to ε_w as the tunnel energy window.

The interesting early time relaxation $1 - m \propto \sqrt{t}$ of an initially magnetized system has been predicted [4], observed experimentally [6], further explained [7], and widely discussed [8]. An unpredicted related phenomenon was later observed by Wernsdorfer *et al.* [9]: the magnetization m of a system of Fe_8 SMM's increases as $\sqrt{t}$, where t is the time after a weak magnetic field is applied to an initially unpolarized system. Conveniently, this latter effect seemed to be independent of system shape. Interesting questions arise: Is this a universal effect to be found in all MQT experiments? If not, on what does it depend? How many time decades does the $\sqrt{t}$ regime cover? What is the final steady-state magnetization? No explanation or simulation that we know of has been offered. We address these questions here.

We report Monte Carlo (MC) results that reproduce the $m \propto \sqrt{t}$ behavior of initially unpolarized systems. We show that this arises from correlations that develop between spins and local magnetic dipolar fields, while cooling to low temperatures, before finally quenching to experiment. Furthermore $m(t)$ depends on the cooling protocol only through the final energy $-\varepsilon_a$ reached just before quenching.

The main results obtained follow. All energies and magnetic fields are given in terms of ε_d and h_d, respectively, where $-2\varepsilon_d$ is the energy of two S spins that lie on sites a distance away, that point along the line joining their two sites, a is the side of a cubic unit cell, $h_d = \varepsilon_d/(g\mu_B S)$, g is the gyromagnetic ratio, and μ_B is the Bohr magneton. We also let σ stand for the rms value of h for a disordered spin configuration [10]. After quenching and applying a field $H \lesssim 1$ at $t = 0$,

$$m(t) \simeq b\varepsilon_a\varepsilon_w H\sigma^{-3} F(\Gamma t, \sigma/\varepsilon_w, \sigma/h_0), \tag{2}$$

where $b \simeq 4\sqrt{2/\pi}$, and

$$F \simeq \Gamma t \quad \text{for } \Gamma t \lesssim 1, \tag{3}$$

$$F \simeq 0.7(\Gamma t)^p \qquad \text{for } 1 \lesssim \Gamma t \lesssim (\sigma/\epsilon_w)^{1/p}, \tag{4}$$

$$F \simeq 0.5\sigma\varepsilon_w^{-1} \quad \text{for } (\sigma/\varepsilon_w)^{1/p} \lesssim \Gamma t, \tag{5}$$

where $h_0 = 2(2\pi)^2/3^{5/2}\rho_v$, ρ_v is the number of spin sites per unit volume, $p \simeq 0.5$, for simple cubic (SC) lattices, and $p \simeq 0.7$ for body centered cubic (bcc) and face centered cubic (fcc) lattices. These results are inferred from MC simulations in which the energy of the magnetic system is held constant in time as well as from arguments given below. For magnetic systems that readily exchange

energy with the lattice, for which the energy is not a constant of time, results are briefly discussed in the closing remarks.

We first describe the simulations. We use the MC method to simulate magnetic relaxation of Ising systems of $\pm S$ spins on simple cubic lattices with periodic boundary conditions, which interact through magnetic dipolar fields and flip under rules to be specified below [11]. The system is first allowed to evolve towards thermal equilibrium at some "high" temperature T_a. We assume $k_B T_a \gtrsim U/10$, which implies that spin reversals then take place mostly through classical thermal processes. Accordingly, spin flips are then governed by detailed balance rules, and Eq. (1) is not enforced. For reasons that are given below, we also impose the restriction $T_a \gtrsim T_0$, where T_0 is the long-range ordering temperature. One may think of this first process as a waiting stage that the systems may have to undergo in the cooling process before quenching to a lower temperature where a tunneling experiment (as in Ref. [9]) can be later performed. Let this first stage end at $t = 0$ with sudden cooling of the system to a "very low" temperature, that is, to a temperature below roughly $0.2U/(Sk_B)$ [3,12]. Accordingly, Eq. (1) is then enforced on all spin flips for $t > 0$. As for a detailed balance, we then proceed as follows. We assume that thermalization of a SMM system with the lattice does not take place (i.e., the energy is constant) at very low temperatures (but see Ref. [13]). We meet this condition by enforcing a detailed balance but using an appropriately chosen pseudotemperature T_u. [From an expression below Eq. (6), $k_B T_u \approx \sigma^2/2\varepsilon_a$. Note that $T_u \geq T_a$, since $-\varepsilon_a$ cannot be smaller than the equilibrium energy at T_a.] We have checked that the mean energy is indeed constant under this rule. We do not report here results we have obtained applying detailed balance rules with $T < T_a$ (applicable to systems where thermal relaxation to the lattice takes place [13]), but we do make a comment on them in the closing remarks. MC results for the time evolution of m/ε_w in SC lattice systems, after a field $H = 1$ is applied upon quenching, are shown in Fig. 1(a) for various values of ε_w. Before quenching, the system was thermalized at $T_a = 10/k_B$ for some time till the energy per spin reached the value -0.58. Clearly, m scales with ε_w up to a crossover time of roughly $10\Gamma^{-1}/\varepsilon_w^2$, where m levels off. Within the time range $1 \lesssim \Gamma t \lesssim 10/\varepsilon_w^2$, $m \propto \sqrt{t}$. Monte Carlo results that show how m scales with ε_a are exhibited in Fig. 1(b) for $\varepsilon_w = 0.1$. Note also that m_e, the leveling off value of m, scales with ε_a, and, as argued below, it scales with σ^{-2} as well, in agreement with Fig. 1(c). Results for different cubic lattices are shown in Fig. 1(c). The log$m$ versus log$t$ slopes in the intermediate time regime are clearly lattice structure dependent. Much of Eqs. (2)–(5) is inferred from these graphs.

For most of the rest of the Letter, we try to understand these results. Let us first examine the physics of the waiting stage. We assume the system is first cooled to some temperature T_a that is above the ordering temperature T_0, but not infinite. We also assume that $k_B T_a \gtrsim U/10$. It then follows from Arrhenius's law, $\tau = \tau_0 \exp(U/k_B T)$, that over barrier spin flipping readily takes place in the laboratory within a second's time if $\tau_0 \lesssim 10^{-5}$ s. Some correlation between spin s_i and field h_i at each site i can therefore be established, but no long-range order can develop if $T_a \gtrsim T_0$. Assume that either $T_a \gg T_0$ or that the time spent in the waiting stage is so short that the probability density function (PDF) $p(h)$ that a randomly chosen site have field h is reasonably approximated by $p(h) \propto \exp(-h^2/2\sigma^2)$. On the other hand, the conditional PDF to find $\pm S$ given a field h acting on the spin fulfills, in equilibrium, $p(\pm S \mid h) \propto \exp(\pm h/k_B T)$. Now, since the joint probability density $p(\pm S, h)$ that, on a randomly chosen site, one find h acting on $\pm S$ is in general given by $p(\pm S, h) = p(\pm S \mid h) p(h)$,

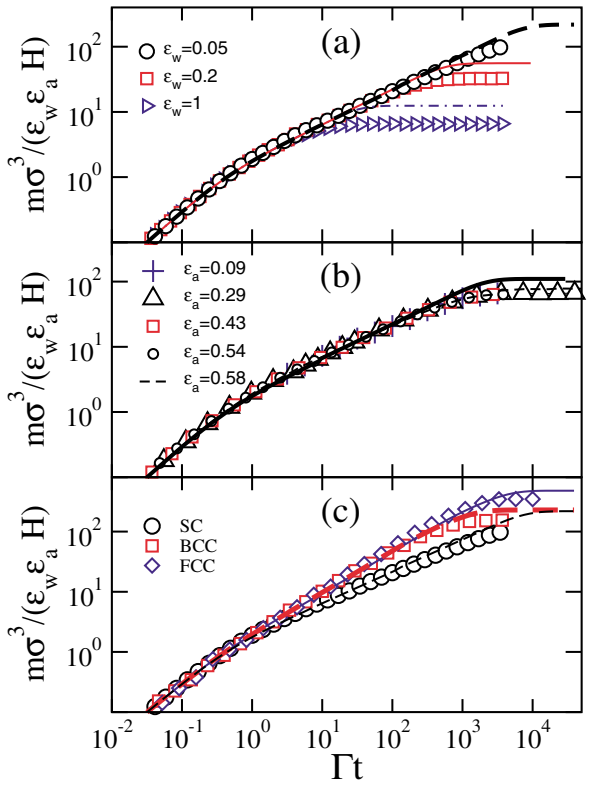

FIG. 1 (color online). (a) m/ε_w versus Γt for an applied external field $H = 1$ for the shown values of ε_w. First, thermalization took place from an initially disordered configuration up to the time when ε_a reached the value 0.58. The dashed, continuous, and dot-dashed lines are for curves calculated from Eq. (11), for $\varepsilon_w = 0.05$, 0.2, and 1, respectively. (b) The same as in (a) but for the shown values of ε_a and $\varepsilon_w = 0.1$. The continuous line is for the solution from Eq. (11). (c) The same as in (a) and (b), but for different lattices, with $\varepsilon_w = 0.05$. For SC, bcc, and fcc lattices, previous partial thermalization took place at $T_a = 10$, 20, and 60, till $\varepsilon_a = 0.31$, 0.28, and 0.53, respectively. The continuous, long dashed, and short dashed lines are for curves calculated from Eq. (11) for fcc, bcc, and SC lattices, respectively. There are no adjustable parameters.

$$p(\pm S, h) \propto e^{-(h\mp\sigma^2/k_BT)^2/2\sigma^2} \tag{6}$$

follows in equilibrium. Therefore, the mean energy is $-\sigma^2/2k_BT$. The replacement $\sigma^2/2k_BT \to \varepsilon_a$, generalizes the above equation to

$$p(\pm S, h) \propto e^{-(h\mp 2\varepsilon_a)^2/2\sigma^2} \tag{7}$$

for all times up to equilibration. Then, to first order in ε_a/σ,

$$p_\uparrow(h) - p_\downarrow(h) \simeq \sqrt{2/\pi} h\varepsilon_a \sigma^{-3} e^{-h^2/2\sigma^2}, \tag{8}$$

where $p_\uparrow(h) = p(S, h)$ and $p_\downarrow(h) = p(-S, h)$. All points for $[p_\uparrow(h) - p_\downarrow(h)]/(h\varepsilon_a)$ obtained from MC calculations collapse onto a single curve in Fig. 2(a), in agreement with Eq. (8). Deviations of higher order in ε_a/σ from Eq. (8) do occur. They are within 10% even if complete thermal equilibration is allowed to take place as long as $T \gtrsim 10$, i.e., above approximately $4T_0$.

We now examine the time evolution of the system after abruptly cooling it, at time $t = 0$, to a temperature below roughly $0.2U/(Sk_B)$. Then, spin flips up to $|S_z| < S$ states can be neglected, and tunneling through the ground state doublet is the only available path for spin reversals. Accordingly, spin flips are allowed only if the spin's Zeeman energy is within the tunnel window. A field H is applied for all $t > 0$. Now, if either the system is in thermal contact with a reservoir at a temperature such that $k_BT \gg \varepsilon_w$ or the energy is constant and sufficiently high such that $k_BT_u \gg \varepsilon_w$, then

$$\dot{m} = 2\Gamma \int dh\, \eta(H + h) f(h, t), \tag{9}$$

where $f(h, t) = p_\downarrow(h, t) - p_\uparrow(h, t)$.

It is worth pointing out that $-f(h, 0)$ is given by Eq. (8), and therefore $f(h, 0) = -(2h\varepsilon_a/\sigma^2)p(h, 0)$ at $t = 0$, where $p(h, 0)$ is the PDF regardless of spin orientation, i.e., $p(h) = p_\downarrow(h) + p_\uparrow(h)$. However, $f(h, t) \propto hp(h, t)$ does *not* hold for $t > 0$. This point is illustrated in Fig. 2(b), where MC results for both $f(h, t)$ and $p(h, t)$ are shown for some nonzero times. $p(h, t)$ is invariant for times $\sim\Gamma$. As reported in Ref. [14], a sharp dip of approximately ε_w half-width does develop in $p(h)$, but only at much later times, and then not when $k_BT \gg \varepsilon_w$. On the other hand, a hole does show up in $f(h, t)$ in Fig. 2(b), as in Wernsdorder's experiments [9], performed at $T =$ 40 mK(which is roughly 10 times as large as ε_w/k_B) [9,14].

The time development of the hole in $f(h, t)$ is illustrated in Fig. 2(c). Note that the hole deepens, but its width remains approximately constant while $\Gamma t \ll 1$, and then, under the conditions stated above Eq. (9), $\dot{f} = -2\Gamma f$. Therefore, since m equals the area covered by the hole {i.e., $m(t) = \int dh\,[f(h, 0) - f(h, t)]$},

$$m \simeq 2\varepsilon_w f(-H, 0)(1 - e^{-2\Gamma t}) \tag{10}$$

if $\Gamma t \ll 1$ and $\varepsilon_w \ll \sigma$. Using Eq. (8), Eq. (3) follows.

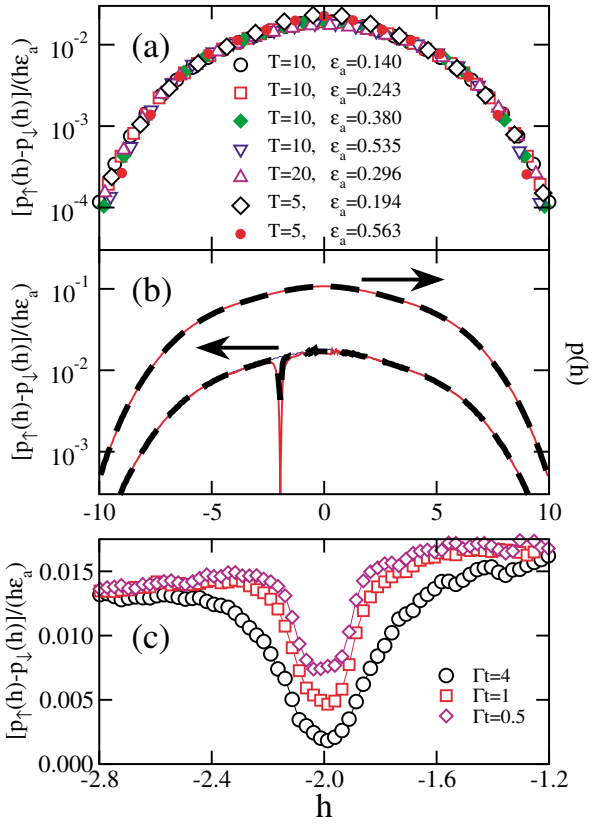

FIG. 2 (color online). $[p_\uparrow(h) - p_\downarrow(h)]/(h\varepsilon_a)$ for a system of $16 \times 16 \times 16$ spins at $T_a = 10$ (recall $T_0 \simeq 2.5$) before quenching. The shown temperatures are given in units of ε_d/k_B. The system was cooled to these high temperatures from an infinite temperature and allowed to thermalize for a time, till the shown energies were reached. All points stand for averages over 1.5×10^5 runs. (b) $[p_\downarrow(h) - p_\uparrow(h)]/(h\varepsilon_a)$ and $p(h) \equiv p_\downarrow(h) + p_\uparrow(h)$ at times $t = 0$, $\Gamma t = 0.62$ (discontinuous line), and $\Gamma t = 2.19$ (continuous line), for the same system as in (a), after the system was first thermalized at $T = 10$ till $\varepsilon_a \simeq 0.25$, was then further cooled to $T = 1$, and $H = 2$ was then applied. A tunnel window $\varepsilon_w = 0.1$ was enforced. All points in (b) stand for averages over 4×10^4 histories. (c) The same as in (b) but for $\Gamma t = 0.5$, 1, and 4; in addition, while $t < 0$, the system had been partially thermalized at $T = 10$ till $\varepsilon_a = 0.247$.

The value m_e that $m(t)$ levels off to after a sufficiently long time, that is, Eq. (5), can be estimated as follows. For $\Gamma t \gtrsim 1$, $f(-H, t) \ll f(-H, 0)$, and the hole becomes only broader, but it cannot become wider than the field distribution $p(h)$. The final area covered by the hole is therefore $\sim 2f(-H, 0)\sigma$, which is the estimated value of m_e, in rough agreement with the expression for m_e below Eq. (5).

More detailed considerations underlie Eq. (4). We have derived [15] the equation

$$\dot{x} \simeq c_1\sqrt{\frac{2}{\pi}} - c_2 \int_0^t d\tau \frac{2\varepsilon_w \dot{x}(\tau)}{\omega(t - \tau) + 2\varepsilon_w}, \tag{11}$$

where c_1 and c_2 are constants to be specified below, $\omega(t - \tau)$ is the inverse of the PDF that the field h on a randomly

chosen site be the same at times t and τ. Quantity m follows from Eq. (11) letting $m = x\varepsilon_a\varepsilon_w H/\sigma^3$, $c_1 = 4$, and $c_2 = 2$. $\omega(t-\tau)$ depends on $t-\tau$ through the probability $\phi(t-\tau)$ that a spin point in opposite directions at times t and τ. To make progress, we make the approximation $\omega \simeq \min[2\pi h_0\phi, 2\sigma\sqrt{\pi}\sqrt{\phi}]$. The approximation for $\phi \ll 1$ follows from the Lorentzian PDF, of half-width $h_0\phi$, that ensues when a small fraction ϕ of sites are randomly occupied by spins [16]. (The two factors of 2 come from the fact that flipping an already present spin S is like placing a $2S$ spin on an unoccupied site.) The approximation for $\phi \sim 1/2$ follows from the Gaussian distribution that holds then. In between, the interpolation checks with our MC results within some 10%. Finally, $\phi(t-\tau)$ must be evaluated. For this purpose, an equation for the fraction of spins $n(t)$ that have flipped at least once before time t is derived [15]. It is Eq. (11) using $n = x\varepsilon_w/\sigma$, $c_1 = 1$, and $c_2 = 1$. We then use $\phi \approx n/2$. The functional dependence of F shown in Eq. (2) follows by careful inspection of these equations. Numerical calculations yield the curves shown in Figs. 1(a)–1(c). The exponent p depends on lattice structure through σ/h_0 in the expression for $\omega(\phi)$ above. The agreement with our MC results exhibited in Fig. 1(c) is reassuring.

A couple of final remarks follow. Equations (2)–(5) are for magnetic systems that do not exchange energy with a heat bath (i.e., the lattice, usually) at very low temperatures. Then, $m(t) \to m_e$ as $t \to \infty$. When heat exchange does takes place readily, as in some systems in Ref. [13], then our simulations show that $m(t)$ eventually crosses over from the value given by Eqs. (2)–(5) to $m_{th}(t) \simeq 0.3(\varepsilon_w/\sigma)^3 H\Gamma t$, for $H \lesssim 1$. This happens when $m_{th}(t)$ becomes the larger of the two. Later on, m_{th} levels off to a quasi-steady-state value (not the final thermal equilibrium value), which depends on both system shape and lattice structure, as expected. (If a field is not applied inmediately upon quenching, but later, the quasi-steady-state value of m_{th} is also affected.) The $(\varepsilon_w/\sigma)^3$ dependence suggests that (see Ref. [11]), in contrast with constant energy magnetization processes, magnetic ordering takes place while the system magnetizes.

Summing up, we have given MC and theoretically based evidence to show that the $m \propto \sqrt{t}$ behavior observed in experiments on Fe_8 clusters [9] after quenching and applying a small field H at $t = 0$ is driven by correlations which are previously established in the system while cooling to very low temperature. We have established that the $\sqrt{t}$ behavior is not universal. More generally, $m(t) \propto t^p$, and p depends on lattice structure. The time range over which this behavior prevails, the value m_e that the magnetization later levels off to, and the crossover time to a final thermally driven regime have been determined. More specifically, Eqs. (2)–(5) have been inferred from MC simulations and Eq. (11), and much of the relevant physics has been explained.

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