Dipolar ordering of molecular magnets

Julio F. Fernández*
ICMA, CSIC and Universidad de Zaragoza, 50009-Zaragoza, Spain
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We simulate the long-time evolution of crystalline systems of molecular magnets (MM's), such as Fe_8 and Mn_{12}, at low temperatures. Then, MM's tunnel as single spins under uniaxial anisotropy energy barriers. Magnetic relaxation of these crystalline systems is controlled by tunneling processes that can be inhibited by magnetic dipolar interactions between different MM's. We study how a generic model of these systems relaxes, from an initially disordered state, towards its ordered equilibrium state below the ordering temperature T_0. Following current theory for tunneling of MM's, spins are allowed to flip in the simulations if the ensuing magnetic dipolar energy change does not exceed some $2\varepsilon_w$ energy bound. It is first shown that whereas the magnetization of spin systems in one dimension ($d=1$), with magnetic dipolar interactions, can relax to its equilibrium value, the energy remains forever far from equilibrium at low temperature if $\varepsilon_w/\varepsilon_d < 3.192\cdots$, where ε_d is a nearest-neighbor dipolar interaction energy. In $d=3$ dimensions, equilibrium does seem to be reached, even if $\varepsilon_w \ll \varepsilon_d$. This conclusion is drawn from long-time evolution results for the energy as well as for spin-spin correlation lengths. However, the relaxation time τ for the approach to equilibrium can become extremely long. More specifically, $\tau^{-1} \approx \Gamma(\varepsilon_w/4\varepsilon_d)^q$ if $\varepsilon_w \lesssim 4\varepsilon_d$, where Γ is a single spin tunneling rate and $q \approx 3$. Finally, the nonequilibrium specific heat C is obtained for both fast and slow temperature sweeping rates dT/dt. In the former case, $C \simeq C_0 T_0/T$, and $C_0/k_B \simeq 0.31(T_0/\tau)dt/dT$. For even a small hint of a singularity to show up at T_0, dT/dt cannot be much larger than $10^{-2}\tau/T_0$.

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I. INTRODUCTION

Quantum tunneling of molecular magnets (MM's) has become a subject of considerable interest. These MM's, such as Mn_{12} and Fe_8, are metal ion clusters within large molecules, which behave as sizable single spins at low temperatures T.[1] They crystallize into systems of nearly isolated spins, which interact only through dipolar fields. These systems are referred to below as dipolarly interacting molecular magnets (DIMM's), or, more simply, as dipolarly interacting spins (DIS's). Crystal-field effects give rise to anisotropy barrier energies U.[2] Tunneling through these barriers takes place in Mn_{12} at $T \sim 0.1\,U/k_B$, where k_B is Boltzmann's constant ($U \approx 55$ K in Mn_{12}).[3,4] Relaxation rates that follow Arrhenius' law[2,5] show that tunneling takes place from thermally excited states at these temperatures. The phenomenon is by now fairly well understood.[6–8] Quantum tunneling of the magnetization (QTM) that is temperature independent has been reported for $T \lesssim 0.1\,U/k_B S$ by various groups ($U \approx 28$ K for Fe_8, and $S=10$ both for Mn_{12} and for Fe_8).[9–13]

Actual observation of this phenomenon had not been widely expected. It had been argued that magnetic dipolar interactions among tunneling spins would lead to Zeemann energy shifts ε_z which would typically exceed the ground state tunnel splitting energy Δ by many orders of magnitude. Thus the vast majority of spins in any given system would not meet the resonant tunneling conditions. The theory of Prokof'ev and Stamp (PS) (Refs. 14 and 15) gets around this difficulty. In it, hyperfine interactions with nuclei provide tunneling (electronic) spins with energies much larger than Δ. More specifically, spins with Zeemann energy ε_z tunnel at rate[16] $\Gamma'(\varepsilon_z) \simeq \Gamma \exp(-\varepsilon_z^2/2\varepsilon_w^2)$, where $\Gamma = \sqrt{\pi/2}\Delta^2/(\hbar\varepsilon_w)$ and ε_w is the typical energy exchanged through hyperfine interactions, which is referred to from here on as the tunnel energy window. In Fe_8 MM's, for instance, values of Δ inferred from experiment (e.g., $\Delta \approx 10^{-7}$ K in Ref. 17) are many orders of magnitude smaller than the typical value, 0.4 K, of ε_z, but over 2% of all spins are expected to be able to tunnel at any one time because $\varepsilon_w \approx 10^{-2}$ K.[18]

The main issues addressed in this paper are next specified. Time relaxation of DIMM's is a collective process. At any one time, only a small fraction of all spins have a Zeemann energy within the energy window ε_w, but as these spins tunnel through their anisotropy energy barriers the magnetic fields they produce at other sites change, bringing some of them into the tunneling window. The question naturally arises: does this process come to a halt before all spins in the system have ever come into the tunnel window if ε_w is sufficiently small? If, on the other hand, this process can go on indefinitely, how does the relaxation time of approach of DIMM's to their low-temperature long-range ordered states[19,20] depend on ε_w? Finally, how do experimentally observable quantities, mainly, the specific heat, change with the observation time in some of these slowly evolving systems. These are the main questions we try to answer in this paper.

It may be worth mentioning that the questions raised in this paper involve very long times, the times necessary for magnetic dipolar field distributions to become spiked as magnetic order sets in. In contrast, the times involved in time relaxation of the magnetization, both from an initially fully magnetized state[14,25–27] and from initially disordered states,[10,11] are much shorter. So is the time necessary for a ''tunnel window imprint'' to develop in field distributions of initially disordered systems.[10,11,18] Hardly any experimental observation of magnetic ordering of DIMM's have thus far been attempted.[21–23] The answers to the questions asked above tell us what relaxation times are to be expected for

Mn_{12}, Fe_8, Mn_6, and for MM's with a wide spectrum of anisotropy energies,[24] and how their long-time behavior will be affected by the application of transverse magnetic fields.

A list of the main results obtained and some comments follow. It is first shown analytically and numerically that the low-temperature equilibrium state of a system of DIS in one dimension can never be reached if $\varepsilon_w < 3.192\cdots\varepsilon_d$, where $2\varepsilon_d$ is the nearest-neighbor dipole interaction energy in one dimension. This result illustrates why eventual ordering of DIS systems in three dimensions with small tunneling windows is not a foregone conclusion. On the other hand, numerical results also show that all spins in one-dimensional (1D) systems do eventually tunnel and that the magnetization can vanish after a fairly short time. Thus the qualitative difference between the often studied short-time magnetization relaxation and the long-time approach to the ordered state that is of interest here is clearly exhibited. For systems of DIS in three dimensions, numerical results for the time evolutions of the energy and of correlation lengths of initially disordered systems are given for various values of ε_w. Equilibrium states (i.e., magnetically ordered states at low temperature or short-range ordered states at high temperatures) are indeed reached in three dimensions long after a relaxation time τ (defined below). The inhibiting effect of a tunnel window is negligible if $\varepsilon_w \gtrsim \varepsilon_c$, where $\varepsilon_c \approx 4\varepsilon_d$, and ε_d is a nearest-neighbor dipole energy (defined below). For $\varepsilon_w < \varepsilon_c$, τ is well fitted by

$$\tau = \Gamma^{-1}\left(\frac{\varepsilon_c}{\varepsilon_w}\right)^q, \tag{1}$$

and $q \approx 3$.[28] The time-dependent specific heat C we obtain from Monte Carlo simulations peaks at the ordering transition temperature T_0 only if the temperature sweeping rate fulfill $dT/dt \lesssim 10^{-2} T_0/\tau$.[29] On the other hand, it turns out that $C \propto 1/T$ if $dT/dt \gtrsim T_0/\tau$. Finally, results for growth of correlation lengths with time give further support to the idea that long-range order is eventually achieved for any nonvanishing tunnel window ε_w. Incidentally, long-distance spin-spin correlations are established along the easy magnetization axis before correlations along perpendicular directions develop at a slower rate.

The plan of the paper is as follows. The model and the method of calculation are discussed in Sec. II. Results for chains of DIS are reported in Sec. III. Time evolutions of the energy E of initially disordered systems obtained for various values of ε_w, from Monte Carlo simulations, are given in Sec. IV. These results are used to define the approach to equilibrium time τ given in Eq. (1). How long-range order grows spatially in time is also shown in Sec. IV. Results for the relaxation of the magnetization of systems that are initially fully polarized, for various values of ε_w, are also given in Sec. IV. A comparison with the much slower approach to thermal equilibrium can thus be made. In Sec. V, numerical results for the time-dependent specific heat C are given. Finally, the results are discussed in Sec. VI.

II. MODEL AND METHOD

The Ising model and the Monte Carlo method used to simulate the long-time behavior of crystalline systems of interacting MM's, their applicability, and other related questions are discussed in this section.

The tunneling rate Γ, the tunnel energy window ε_w, and how readily energy can be exchanged with a phonon bath are the things that matter for the physics under consideration: the long-time evolution of a DIMM's. Since any one given spin tunnels at a negligible rate as long as $|\varepsilon_z| \gg \varepsilon_w$, the following simplifying assumption is made here throughout: tunneling proceeds at a fixed rate Γ if $|\varepsilon_z| < \varepsilon_w$, but not at all if $|\varepsilon_z| > \varepsilon_w$.[30]

How readily the system can exchange energy with a heat bath does matter for the approach to equilibrium, but this question is beyond the scope of this paper. Ordering of DIMM's at very low temperatures, which can only occur if heat is exchanged, takes place readily. Thermal contact with a heat reservoir at some temperature T is assumed in this paper.[22,23] More specifically, detailed balance holds in all the simulations reported here, that is, if upon flipping a spin's energy changes by ΔE and $|\Delta E| < 2\varepsilon_w$, then the ratio between the forward and backward probabilities for it is $\exp(-\Delta E/k_B T)$.

An Ising model of $S = \pm 1$ spins that interact through dipolar fields is chosen for the simulation of a crystalline system of MM's. It is the drastic but reasonable simplification that is usually made.[25,26] Simulation of tunneling through a uniaxial anisotropy barrier U by flipping $S = \pm 1$ Ising spins is reasonable for $T \lesssim 0.1U/k_B S$, since only the *two* states $S_z = \pm S$ are occupied then with a nonnegligible probability.[25,26] In the present model, all sites on a simple cubic (sc) lattice are occupied by $S = \pm 1$ spins. It is expected that the answer to the rather generic question being addressed in this paper does not depend on lattice type, and that it applies to Fe_8, Mn_{12}, as well as to other crystals of MM's.[24]

To complete the model's definition, let the field at site i be

$$h_i = h_d \sum_j (a/r_{ij})^3 (1 - 3z_{ij}^2/r_{ij}^2) S_j, \tag{2}$$

where r_{ij} is the distance between the i and j sites, a is the sc lattice constant, z_{ij} is the z component of r_{ij}, and the sum is over all j sites of the system except $j = i$. Unless otherwise specified, periodic boundary conditions (PBC's) are used throughout. Then r_{ij} is the distance between i and the nearest image of site j. The interaction energy is given by

$$E = \frac{\varepsilon_d}{2h_d} \sum_i h_i S_i, \tag{3}$$

where the sum is over all lattice sites i. Contact with an S spin MM's crystal is made letting $\varepsilon_d = (\mu_0/4\pi) \times (g\mu_B S)^2/a^3$, where g is the gyromagnetic ratio, μ_B is the Bohr magneton, and μ_0 is the vacuum permeability. Equivalently, $\varepsilon_d \simeq 0.622(gS)^2(1\ \text{Å}/a)^3$ K.

The phenomenon under consideration is a collective effect. Therefore a reliable numerical approach is called for. The Metropolis version of the Monte Carlo (MC) algorithm

seems best suited for this purpose and is therefore used throughout. The usual Monte Carlo updating procedure, which is adopted here, is next justified for DIMM's. The dipolar field acting on all spins in the system is updated whenever a spin flips. Any variation of the field h_i acting on spin S_i while S_i tunnels is disregarded in this model. This effect is next estimated for a disordered state. Note first that dh_i/dt is given by the time derivative of Eq. (2). Let f be the fraction of spins within the tunneling energy window, which, using a Gaussian distribution of local fields with variance σ^2, gives $f \simeq \sqrt{2/\pi}\,(\varepsilon_w h_d/\sigma\varepsilon_d)$ if $\varepsilon_w \ll \sigma(\varepsilon_d/h_d)$. Replacement of dS_i/dt by $\eta_i f\Gamma$, where $\eta_i = \pm 1$ randomly, in the equation that follows from taking the time derivative of Eq. (2), gives $\langle (dh_i/dt)^2\rangle \simeq (2/\pi)(h_d\Gamma\varepsilon_w/\varepsilon_d)^2$. Since the variation δh_i of h_i while S_i tunnels is roughly $\Gamma^{-1}dh_i/dt$, it follows that $\delta h_i \sim \varepsilon_w(h_d/\varepsilon_d)$. That is, δh_i is comparable to the tunnel "field window." This simple result shows that, while the effect is not negligible, it may, as in the spin tunneling theory of Prokof'ev and Stamp,[14] be reasonably disregarded.[31]

In order to characterize how long-range order is established, two quantities are next defined,

$$\xi_z \equiv \sum_{n\neq 0, n\in \mathbf{c0}} \langle S_0 S_n\rangle, \tag{4}$$

where the sum is over all spins on sites $n \neq 0$ that lie on the column **c0** that contains site 0, and

$$\xi_x^2 \equiv \sum_{j\neq 0, j\in \mathbf{p0}} \langle S_0 S_j\rangle, \tag{5}$$

where the sum is over all spins on sites $j \neq 0$ that lie on the plane **p0** that contains site 0 and is perpendicular to the z axis. Quantity ξ_z and ξ_x are measures of spin-spin correlation lengths along the z direction and on planes perpendicular to the z direction, respectively.

All results quoted below are for systems with PBC's, unless stated otherwise. Whereas time evolutions of the magnetization of systems that are initially fully polarized can be quite different for PBC's and free boundary conditions (FBC's), evolutions of the energy and correlation lengths of initially disordered systems, on the other hand, are nearly the same for both boundary conditions.

Unless it is otherwise specified, all magnetic fields and energies are given in terms of h_d and ε_d, respectively, -and time is given as the number of Monte Carlo (MC) sweeps. Simple tunneling probability considerations for a spin with equal initial and final Zeeman energies lead to the following rule: (MC sweeps)/Γ is the corresponding experimental time. Accordingly, Γt and the number of MC sweeps (MCS's) are used below indistinguishably. Temperatures are given in terms of ε_d/k_B, unless they are explicitly expressed in terms of the ordering temperature, which is given by $T_0 \simeq 2.5\varepsilon_d/k_B$ for a simple cubic lattice.[19]

III. LOW DIMENSIONS

The number of domains in one dimension is shown in this section to be a constant of time if $\varepsilon_w/\varepsilon_d < 3.192\cdots$. Numerical results are also obtained for time evolutions of the energy and of the magnetization.

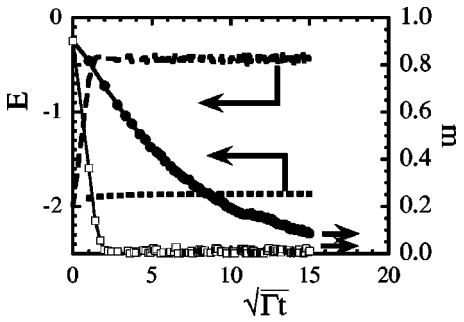

FIG. 1. Energy E and magnetization m versus $\sqrt{\Gamma t}$ for two spin chains at $T = 10\varepsilon_d/k_B$, one for $\varepsilon_w = 2\varepsilon_d$, the other one for $\varepsilon_w = 20\varepsilon_d$. Γt is the number of Monte Carlo sweeps. For E, the dotted and dashed lines are for $\varepsilon_w = 2\varepsilon_d$ and $20\varepsilon_d$, respectively. Near complete initial order gives an initially small value of E (the ground-state energy is $-2.40\varepsilon_d$). For $\varepsilon_w = 20\varepsilon_d$, disorder quickly sets in. Since T is large, but not infinite, E increases up to its equilibrium value ($-0.44\varepsilon_d$), but does not vanish. For $\varepsilon_w = 2\varepsilon_d$, the value of E reamins nearly constant in time. For m, ● and □ stand for $\varepsilon_w = 2\varepsilon_d$ and $20\varepsilon_d$, respectively, and the lines are guides to the eye. Initially, $m = 0.9$. Data points for $\varepsilon_w = 2\varepsilon_d$ and $20\varepsilon_d$ stand for averages over 10^3 and 10^2 different Monte Carlo runs, respectively.

Unless the system is rather polarized (approximately above 80%), numerical simulations show that *all* spins in 1D Ising chains do eventually come into the tunneling energy window and the magnetization reaches its equilibrium value if $\varepsilon_w \gtrsim 0.2\varepsilon_d$. On the other hand, the energy remains permanently far away from the equilibrium value if $\varepsilon_w/\varepsilon_d \lesssim 3.2$. This behavior is illustrated in Fig. 1. There is of course no contradiction between these two results: the number of domains can remain constant while their boundaries shift about, thus restricting energy variations while allowing all spins to flip. Incidently, the magnetization exhibits in Fig. 1 a $\sqrt{t}$ short-time relaxation, much as in three dimensions.[25–27]

The time invariance of the number of domains is next shown. In order to either create a new domain or destroy an existing one, a spin that is flanked by two nearest neighbors that are both pointing in the same direction must be flipped (else, a spin flip corresponds to a domain boundary move). The magnitude of the field acting on such a spin takes on its minimum value if all spins beyond the nearest neighbors are antiparallel to the latter. This minimum value is given by $4h_d(1-\Sigma_{n\geq 2}n^{-3})$, as follows immediately from Eq. (2). Now, since $\Sigma_{n\geq 2}n^{-3} = 0.202\cdots$,[32] it follows then that the number of domains in one dimension is constant in time if $\varepsilon_w/\varepsilon_d < 3.192\cdots$.

Numerically obtained spin-spin correlation lengths ξ_z^∞ in the $t\to\infty$ limit are plotted in Fig. 2 versus ε_w. In accordance with the analytic result above for domain number invariance, for $\varepsilon_w/\varepsilon_d \lesssim 3.2$, ξ_z remains in time considerably smaller than the equilibrium value, which is achieved if $\varepsilon_w/\varepsilon_d \gtrsim 3.2$.

IV. TIME SCALE AND APPROACH TO EQUILIBRIUM IN THREE DIMENSIONS

The time evolution of the energy E was obtained for various values of ε_w and of the temperature. Initially, E is linear

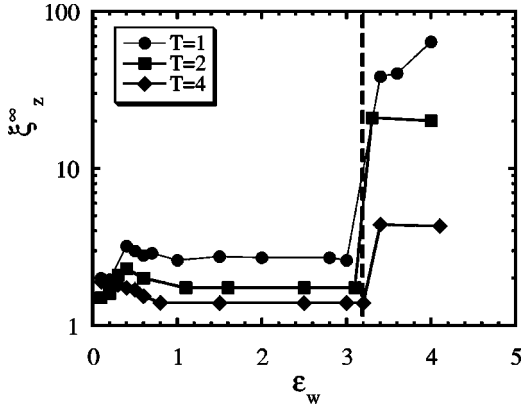

FIG. 2. Stationary value ξ_z^∞ of the correlation length ξ_z along the z axis, obtained after a sufficiently long time, versus ε_w for the shown values of T. For values ε_w that are to the left of the dashed line, the number of domains is conserved. These data points come from systems of 64 spins. Only the data points shown for $\varepsilon_w > 3.2\varepsilon_d$ and $T=1$ seem to suffer from size effects. All lines are intended as guides to the eye.

in the time t. Let E_0 be the ground-state energy, which is approximately $-2.7\varepsilon_d$.[19] The relaxation time τ is defined through the relation, $E/E_0 \simeq t/\tau$, which seems to be valid for $E/E_0 \lesssim 0.1$. Data points obtained for $T=1$ and various values of ε_w are shown in Fig. 3.

Inspection of data points for, say, $\varepsilon_w = 0.4\varepsilon_d$ in Fig. 3 raises the question of whether E settles in a steady-state value before its equilibrium value is reached. The plot of E versus t/τ in the inset, on a much longer time scale, shows that this is not so. For $t/\tau \gtrsim 10$, E seems to relax to its equilibrium value logarithmically in time.

All data points shown in Fig. 3 for $\varepsilon_w \geqslant 0.4\varepsilon_d$ are for systems of $8\times8\times8$ spins with PBC's. Results for cubic systems with FBC's differ by only a few percent. For $\varepsilon_w = 0.1\varepsilon_d$, data points are shown both for systems of $8\times8\times8$ and of $16\times16\times16$ spins. No size effects are observed. Only data points for systems of $16\times16\times16$ spins are shown

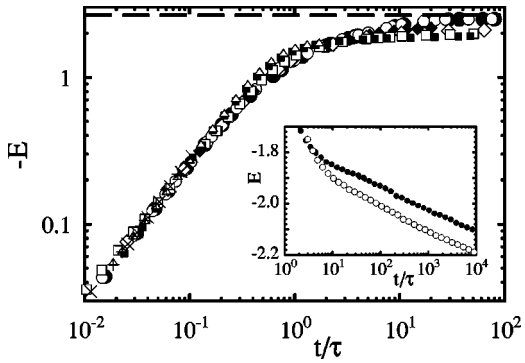

FIG. 3. (a) Energy versus t/τ at $T=1$ for various values of ε_w. ●, ○, ♦, ◇, □, ■, and △ stand for systems of $8\times8\times8$ spins with $\varepsilon_w/\varepsilon_d = 20$, 8, 3, 2, 1, 0.4, and 0.1, respectively. + and × stand for systems of $16\times16\times16$ spins and $\varepsilon_w/\varepsilon_d = 0.1$ and 0.05, respectively. The dashed line stands for the ground-state energy. A plot of E versus t/τ, on larger time scale, is shown in the inset for $\varepsilon_w = 0.4\varepsilon_d$ (●) and $\varepsilon_w = \varepsilon_d$ (○).

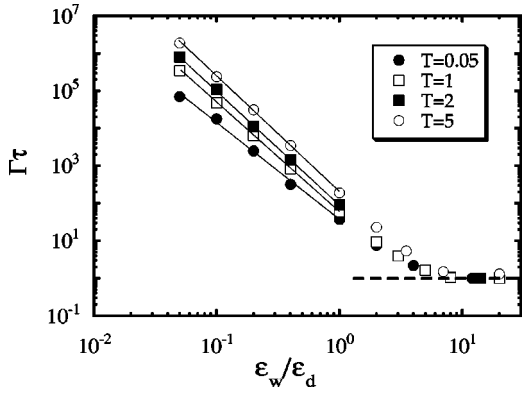

FIG. 4. Data points of $\Gamma\tau$ versus $\varepsilon_w/\varepsilon_d$ for the shown temperatures. The symbols shown for the data points are approximately as large as the corresponding errors. The sloping straight lines are for the fits given by Eq. (1), and the horizontal one is for the $\varepsilon_w \to \infty$ asymptotic behavior.

for $\varepsilon_w = 0.05\varepsilon_d$. For such small values of ε_w and systems of only $8\times8\times8$ spins, the number of spins within the tunnel window is too small to afford good statistics.

Time evolutions of the energy have also been performed

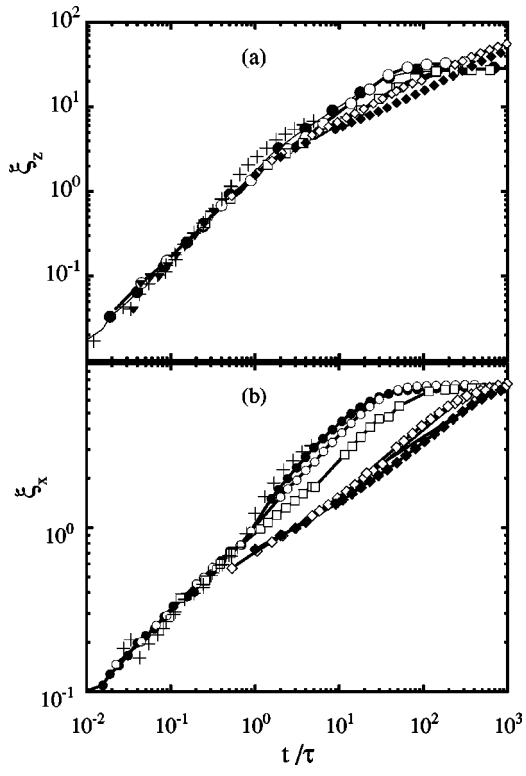

FIG. 5. (a) Correlation length ξ_z versus reduced time t/τ for various ε_w at $T=1$. [τ is given by Eq. (1).] ▼ stands for an average over 40 runs for a system of $16\times16\times16$ spins and $\varepsilon_w = 0.05\varepsilon_d$. All other data points are for averages over at least 100 runs. + is for $8\times8\times16$ spins with $\varepsilon_w = 0.1\varepsilon_d$. All other data points are for systems of $8\times8\times64$ spins. ●, ○, □, ◇, and ♦ stand for $\varepsilon_w/\varepsilon_d = 0.4$, 1, 2, 4, and 20, respectively. (b) Same as (a) but for ξ_x. Statistics of data points for $\varepsilon_w = 0.05\varepsilon_d$ are too poor to be worth showing.

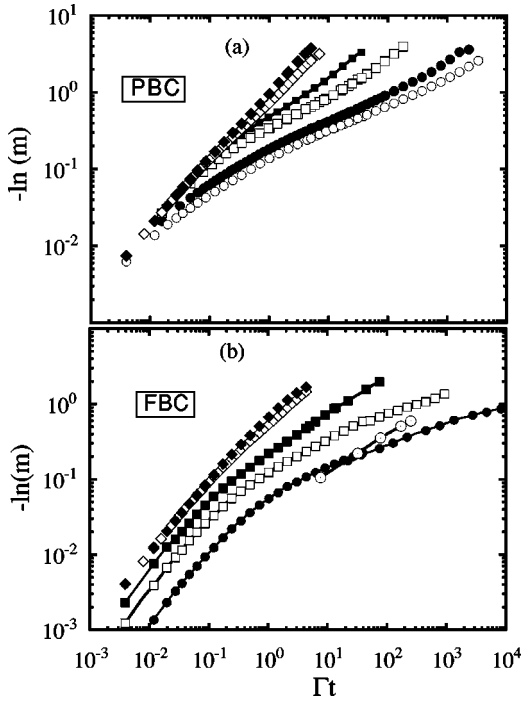

FIG. 6. (a) Log-log plot of $-\ln(m)$ versus time for cubic systems at $T=1$ with PBC's that are initially fully polarized, i.e., $m=1$. ○, ●, □, ■, ◇, and ◆, stand for $\varepsilon_w/\varepsilon_d=0.05$, 0.1, 0.4, 1, 3, and 20. All data points stand for averages over at least 40 MC simulations of systems of $16\times16\times16$ spins. (b) Same as in (a) but for FBC's. No (○) data for $\varepsilon_w/\varepsilon_d=0.05$ are shown. Experimental data from Ref. 9 are shown as ⊙, assuming $\Gamma=10^{-2}$ s^{-1}.

for other values of the temperature, and τ values have been drawn from the results obtained. Plots of $\Gamma\tau$ versus ε_w are exhibited in Fig. 4 for various temperatures. For $\varepsilon_w \gtrsim 4\varepsilon_d$, $\tau \simeq \Gamma^{-1}$. The data for $\varepsilon_w \lesssim 4\varepsilon_d$ and each temperature are fitted rather well with Eq. (1), where ε_c and q vary somewhat with T, from $\varepsilon_c=2.6\varepsilon_d$ and $q=4.1$ for $T=0.05$ up to $\varepsilon_c=5.6\varepsilon_d$ and $q=3.1$ for $T=5$.

Plots of ξ_z and ξ_x versus t/τ are shown in Figs. 5(a) and (b) for $T=1$ and various values of ε_w. Furthermore, data (not shown) obtained for various values of L_x but the same value of L_z are consistent with growth of ξ_z that is approximately independently of L_x for all the values of $L_x=L_y \geqslant 4$ we have tried. This gives further support to the conclusion that, in contrast with one dimension, no bound on the growth of magnetic long-range order seems to exist in three dimensions.

Numerical results for the relaxation of the magnetization m of initially fully magnetized ($m=1$) systems of $16\times16\times16$ spins are given in Figs. 6(a) and (b) for PBC's and FBC's, respectively, for various values of ε_w. Analogous results have been obtained[25,26] and debated before.[27] Figures 6(a) and (b) are only given in order to illustrate the great difference between the magnetization and the energy relaxation.

V. TIME-DEPENDENT SPECIFIC HEAT

Results obtained for the time-dependent specific heat, under various temperature sweeping rates dT/dt, are reported

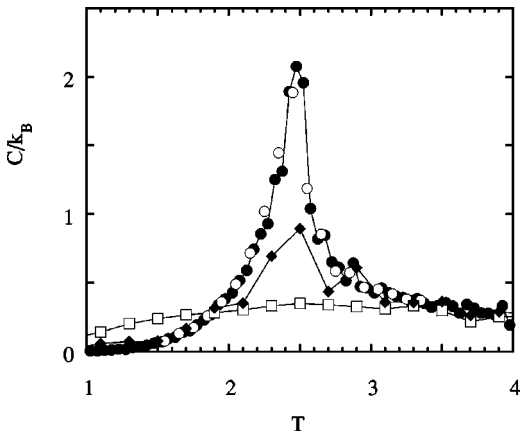

FIG. 7. Specific heat versus temperature for systems of $L_x\times L_y\times L_z$ spins. All temperature sweeps started at $T=2T_0$. ● and ○ stand for equilibrium values for systems of $16\times16\times16$ and $8\times8\times16$ spins, respectively. ◆ and □ stand for data points obtained from runs of 8×10^5 and 10^5 MC sweeps for systems of $16\times16\times16$ and $8\times8\times16$, respectively, with $\varepsilon_w=0.1\varepsilon_d$. Each □ data point stands for an averages over 100 MC runs. ◆ stand for single runs. Lines are shown as guides to the eye.

in this section. Data points for $\varepsilon_w=0.1\varepsilon_d$ and two very slow rates, 10^5 and 8×10^5 MC sweeps per data point, are shown in Fig. 7. Since the temperature was changed in steps of 0.2, i.e., $0.08\,T_0$, and $\Gamma\tau\approx10^5$ (from Fig. 4), $\Delta T/\Delta t \approx 10^{-1}\,T_0/\tau$ and $\Delta T/\Delta t \simeq 10^{-2}T_0/\tau$ are the corresponding values of the sweeping rates. Equilibrium values are also given in Fig. 7. The agreement shown between data points for systems of $16\times16\times16$ and of $8\times8\times16$ spins in equilibrium suggests that size effects are small here.

Semilog plots of the energy versus temperature obtained for various fast sweeping rates satisfying $1\lesssim(\tau/T_0)dT/dt$ are shown in Fig. 8 for $\varepsilon_w=0.1\varepsilon_d$. As expected, not even a hint of a phase transition is observed in the specific heat for such fast temperature sweeping rates. Since $E\propto\ln(T)$ seems

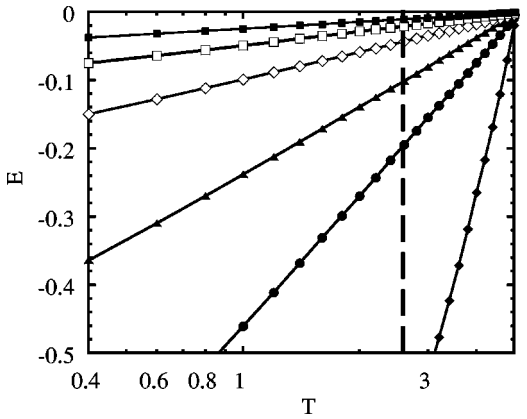

FIG. 8. Semilog plots of the energy E versus temperature for systems of $8\times8\times16$ spins. ■, □, ◇, ▲, ●, and ◆ stand for $(\tau/T_0)dT/dt\simeq76.8$, 38.4, 19.2, 7.68, 3.84, and 0.96, respectively. The vertical dotted line is at the transition temperature. All temperature sweeps started at $T=2T_0$. Lines are shown as guides to the eye.

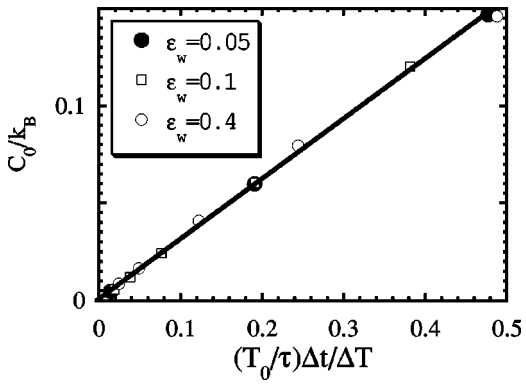

FIG. 9. C_0/k_B versus the inverse temperature sweeping rate $(T_0/\tau)dt/dT$ for the shown values of ε_w (in terms of ε_d). A straight-line fit is also shown.

to hold approximately for each curve, the relation

$$C \simeq C_0 \frac{T_0}{T}, \tag{6}$$

where C_0 is the specific heat at temperature T_0, follows. This relation differs from the one, $C \propto 1/T^2$, that might have been expected from the first term in an infinite T series expansion for the equilibrium specific heat. Similar results have been obtained for $\varepsilon_w = 0.05\varepsilon_d$ and for $\varepsilon_w = 0.4\varepsilon_d$. Data points for C_0 obtained for these three values of ε_w are plotted versus $(T_0/\tau)dt/dT$ in Fig. 9. The relation

$$\frac{C_0}{k_B} \simeq 0.31 \frac{T_0}{\tau} \frac{dt}{dT} \tag{7}$$

follows from the straight-line fit shown in Fig. 9.

VI. CONCLUSIONS

Monte Carlo simulation results show that low-temperature ordered states are reached after sufficiently long times by systems of spins, with dipolar interactions, on 3D lattices. This was shown for values of ε_w as small as $0.1\varepsilon_d$. This is in strong contrast with the behavior of 1D systems, in which the number of domains was shown to be a constant of time if $\varepsilon_w/\varepsilon_d < 3.192\cdots$.

For three dimensions, a relaxation time τ of approach to thermal equilibrium has been defined and found to depend on the tunneling rate Γ and on the tunnel energy window ε_w as follows. For $\varepsilon_w \gtrsim 4\varepsilon_d$, the inhibiting effect of a tunnel window is negligible and $\tau \simeq \Gamma^{-1}$. This is roughly to be expected since the rms dipolar energy of a completely random spin system in a simple cubic lattice is $3.655\varepsilon_d$. On the other hand, for $\varepsilon_w \lesssim 4\varepsilon_d$, τ is given by Eq. (1). Thus τ can be very long. Furthermore, τ is much more sensitive than the magnetization relaxation[25–27] to the value of the tunnel energy window, as illustrated in Sec. IV. No explanation is offered for the approximately $\tau \propto 1/\varepsilon_w^3$ behavior.

The time-dependent specific heat C we obtain from Monte Carlo simulations peaks at the ordering transition temperature T_0, as shown in Fig. 8, only if the temperature sweeping rate fulfills $dT/dt \lesssim 10^{-2} T_0/\tau$. Recent experiments[23] on Mn_6 yield a specific heat that peaks slightly at T_0. Thus the inequality $dT/dt \lesssim 10^{-2} T_0/\tau$ is likely fulfilled, though this is not known for certain because the value of Γ, and hence of τ, is unknown for Mn_6. Considerably slower than $10^{-2} T_0/\tau$ rates are necessary to closely approach the equilibrium specific-heat singularity at T_0. On the other hand, it turns out that $C \simeq C_0 T_0/T$ if $dT/dt \gtrsim T_0/\tau$, where C_0 depends on the sweeping rate according to Eq. (7).

All MC simulations were performed on a personal computer running at 1 GHz. No set of data points shown for any group of evolution histories required over a week of a single computer processor's time.

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*Electronic address: JFF@Pipe.Unizar. Es

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