Monte Carlo simulations of an Ising-like model for photoinduced spin-state switching in nanoparticles of transition metal complexes

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Abstract. We investigated the switching behavior of small particles of an Ising-like model under constant excitation by means of Monte Carlo simulations to study photoinduced spin-state switching in nanoparticles of transition metal complexes. The threshold intensity required for that switching becomes drastically small in small particles with diameter of less than 10 pseudospins. This lower intensity results enhancement of the pseudospin fluctuation at the surface in the small particles. Our result might originate the increase of the photoinduced magnetization in nanoparticles of a Mo-Cu cyanide.

1. Introduction
Ising-like models and similar ones have been investigated for spin-state switching of the bulk of the transition-metal complexes [1-17]. The main targets are cyano-bridged transition metal complexes and Fe(II) spin-crossover complexes. In such materials, the spin state of transition metals is controlled by external stimuli, e.g. heating/cooling [3, 18], applying pressure [12], magnetic field [19], and irradiation [20-26]. Recently, the photoinduced spin-state switching in nanoparticles of these complexes has been reported [27, 28], as well as the thermal induced one [29]. We studied the switching behavior of small clusters of Ising-like pseudospins under constant excitation to elucidate photoinduced switching in nanoparticles.

Experimentally, photoinduced increase of magnetization of nanocomposites of Co-Fe cyanide and silica was observed [27], whereby Co-Fe cyanide forms nanoparticle crystalline structures of 8–10 nm. A photoinduced effect in nanoparticles of Mo-Cu cyanides coated with polymers has also been reported [28]. It is interesting that the magnetization after irradiation in nanoparticles is greater than that of the bulk. Such enhanced magnetization is likely to indicate small-size effect of the sample. This study is intended to predict a small-size effect in photoinduced switching from a theoretical study with the Ising-like model for simulating various observations.

2. Method
The Ising-like model that we use represents bistable local states accompanied by lattice distortions. A schematic adiabatic potential diagram for such bistable states is shown in figure 1(a) with a configuration coordinate $u_i$ representing the variation of atomic positions. The two local energy minima separated by an energy barrier correspond to two different states,
L and H, corresponding to low-spin and high-spin states in the transition metal complexes with a spin-state bistability. If the system energy is determined mostly by the two states, we can use the discrete pseudospin variable \( S_i \) instead of the continuous variable \( u_i \). The former takes the respective values of -1 and 1 for states L and H, as shown in figure 1 (b). A small particle is simplified into a cluster of a pseudospin lattice, as shown in figure 1(c).

In this model, the system energy is expressed as

\[
H = - \sum_{(i,j)=\text{NN}} J_{ij} S_i S_j + \sum_i \frac{\Delta_i}{2} S_i,
\]

where the ‘pseudospin’ variable \( S_i = \pm 1 \) denote the two states (L and H) of the site \( i \). In this paper, these states are assumed for simplicity as energetically degenerated: \( \Delta_i = 0 \) for all pseudospins. The nearest neighbor (NN) coupling \( J_{ij} \) is assumed to be a positive constant \( J \), so that the neighbouring sites prefer to be in the same state. Because the temperature is fixed as \( k_B T = J \), we do not consider that the phenomenological temperature dependent term is often implemented in the Hamiltonian [5, 9].

We investigated spherical particles with size \( N \), denoted as \( P_N \), for various diameters \( N \). For comparison, we also calculated a cubic lattice with a three-dimensional periodic boundary condition, denoted as \( B_N \), which has often been used for bulk analyses.

We have used a classical Monte Carlo simulation [30] to study model kinetics at finite temperatures under external excitations, corresponding to photoexcitation. In those simulations, the flipping rate at each pseudospin \( j \) is the sum of the thermal and external terms: \( w_j = w^T_j + w^P_j \). When we consider selective excitation from L to H, we set \( w^P_j (L \rightarrow H) = W \) and \( w^P_j (H \rightarrow L) = 0 \). For thermal flipping rate \( w^T_j \), we used a heat bath model: \( w^T_j (S_j) = 1/\{\exp(\beta \Delta E_j) + 1\} \), where \( \Delta E_j \) gives a change in the energy of the system if the spin flip at the \( j \)-th unit is flipped, and \( \beta = 1/k_B T \) [31]. In each Monte Carlo step (MCS), both thermal and external spin-flip trials are performed at every site once on average. The heat bath model
Figure 2. Monte Carlo simulation on the kinetics of the excitation-induced phase transition in small particles and in a periodic lattice. (a) The fraction of converted sites as a function of the excitation time $t$ in Monte Carlo steps (MCS) with $W = 0.09 / \text{MCS}$ at $k_B T = J$. $P_N$ and $B_N$ respectively indicates a spherical particle with size $N$, and a periodic $N \times N \times N$ lattice. (b) The converted fraction in the $P_{10}$ particle for $W = 0.09$ per MCS, at $k_B T = J$. The solid line shows the total fraction. Broken and dotted ones respectively represent the partial fractions of the surface and inside pseudospins.

3. Result
Suppose the system is initially in the L phase and develops under an excitation rate $W$ from L to H. Figure 2(a) shows the fraction of pseudospins in the H state, $n_H$, as a function of the excitation time $t$ with the excitation intensity $W = 0.09 / \text{MCS}$ in the $P_5$, $P_{10}$, and $B_{48}$. Conversion to the H phase occurs only in the particles. In particular, the smallest particles $P_5$ switch fastest. In the periodic system $B_{48}$, in contrast, $n_H$ retains a small value, indicating no switching.

In the Ising-like model with constant excitation, switching occurs only by strong excitation, i.e. a threshold intensity of the excitation exists. These results indicate that the threshold intensity is smaller than $0.09 / \text{MCS}$ for nanoparticles and larger for the periodic system.

Switching even under weaker excitation is attributable to a surface effect. To clarify this mechanism, the time development of partial fraction of $n_H$ is shown in figure 2(b). The ‘inside’ and ‘surface’ parts respectively denote the units surrounded by six neighbours and the others. In the initial stage of switching, $n_H$ is larger in the surface region, indicating that an HS nucleation phase occurs at the surface. The units at the surface only have less than six neighbours, generating large fluctuations of the spin-states. Consequently, nucleation occurs even under weak excitation at the surface, resulting in the rapid switching in the small particles with a large surface.

We calculated the size-dependence of the threshold intensity $W_c$. To obtain $W_c$, we first calculate the switching period $t_c(W)$, the excitation time required for the switching with the excitation rate $W$. After that $W_c$ is obtained as the $W$ with which the $t_c(W)$ exceeds 10000...
MCS. The calculated $W_c$ is shown in figure 3, in which we found two important features. One is the drastic decrease of $W_c$ in very small particles, e.g. $W_c = 0.025$ /MCS for $P_5$. This decrease is attributable to the fractional increase of pseudospins at the surface, e.g. 79% in $P_5$ particles. The other is that $W_c$ of $P_N$ for any $N$ is smaller than that of the periodic lattice. In the case of a periodic lattice with the same parameters, the threshold is calculated as $W_c = 0.105$ /MCS [32, 33, 31]. The surface exists even in large particles, engendering smaller $W_c$ than the bulk.

4. Discussion

We found that the threshold intensity required for photoinduced switching is reduced drastically in the small particles. The mechanism is rapid nucleation at the surface. We have demonstrated similar accelerated photoinduced switching in a superlattice [31, 32, 33], where the origin is also the rapid nucleation in a part of the sample. To induce the rapid switching, it is most efficient to implement the part where the nucleation occurs easily.

In experiments, the raising excitation intensity is limited to avoid other structural changes such as melting. Our result indicates the possibility that the small particles, even consisting of the system exhibiting no switching in the crystal, can switch by available irradiation. For example, a Mo(CN)$_8$Cu$_2$ complex is one candidate. Both bulk and particles of this material exhibit photomagnetism [25, 28, 34], but only 75% of the switching process occurs in the bulk compound as compared to the nanoparticles [28]. The authors of the experimental report describe that the enhancement in nanoparticles results from better light penetration in the nanoparticle film than that of the bulk. We suggest another model with our simulations: a smaller threshold intensity of the nanoparticle than the bulk. Further theoretical and experimental studies are required to clarify the mechanism of this enhanced photomagnetism. In particular, existence of a cooperative effect should be examined because our theory is based on cooperative interaction among units.
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