Simulation of Non-equilibrium Phase Transition in a Random Magnetic System

Tamotsu Kitazaki and Tomohiko Kato
Fukuoka institute of Technology, Higashi-ku, Fukuoka 811-0295, Japan
E-mail: ad08001@bene.fit.ac.jp

Abstract. The time-dependent phase transition of a random magnetic system is investigated using a dynamic Monte Carlo simulation. The present random system is a simple dilution of magnetic atoms with Ising spins in a square lattice. The time-dependent order parameters are calculated as a function of temperature for several concentrations of magnetic atoms. The results indicate that as the averaging time becomes shorter, the phase transition becomes more gradual. This tendency is most pronounced around the percolation concentration. These results are compared to results of a recent NMR spin echo experiment on Mn$_x$Cd$_{1-x}$(HCOO)$_2$·2(NH$_2$)$_2$CO reported by Kubo et al. (2007). Although the present simulation includes essentially no adjustable parameter, the results are in satisfactory agreement.

1. Introduction
Phase transitions of random magnetic mixtures often exhibit gradual transitions in which critical transition points are rarely assigned. These phase transitions are essentially non-equilibrium phenomena because the relaxation times of large magnetic clusters become longer than the observation time in the critical region. A gradual phase transition was observed in an NMR spin echo experiment on Mn$_x$Cd$_{1-x}$(HCOO)$_2$·2(NH$_2$)$_2$CO by Zenmyo et al. [1] for various concentrations of Mn atoms with a fixed observation time of $10^4$ seconds, and, in another study on this experiment, Kubo et al. [2] reported the temperature dependence of order parameters with changing observation time.

In the present study, the temperature dependences of the order parameters are calculated as a function of observation time using a dynamic Monte Carlo simulation [3]. The calculated results are compared to the experimental results mentioned above. Preliminary calculations were reported in [4].

2. Model and method of simulation
2.1. Model
In the present study, we treat a system in which magnetic and non-magnetic atoms are located randomly in a square (500x500) lattice. Magnetic atoms are assumed to be Ising spins that interact by a ferromagnetic exchange interaction $J$ with only the nearest neighbor sites. This model is employed in analyzing the experiment on the real compound Mn$_x$Cd$_{1-x}$(HCOO)$_2$·2(NH$_2$)$_2$CO, which is a rare observation on the time dependence of order parameters. In this compound, however, Mn atoms behave as Heisenberg type spin of magnitude 5/2 on a quasi-two dimensional (square) lattice. The magnetic structure in low temperature is anti-ferromagnetism. Because of the difference between the present model and the real compound, we do not expect a quantitative agreement, but expect for the...
simulation to reproduce the general feature of the experiment. Note that the present calculation for ferromagnetism is available for the anti-ferromagnetic system in the spin 1/2 Ising model.

2.2. Dynamic Monte Carlo simulation
In conventional Monte Carlo simulations, time is counted in Monte Carlo steps (MCS) that do not correspond to actual time. The dynamic Monte Carlo simulation [3], however, uses transition probabilities, so that the time corresponds to actual time.

In the dynamic Monte Carlo simulation, the Poisson process is assumed, and so the transition time is given by \( t_c = -(1/W_i) \log r \), where \( W_i \) is the total transition probability that any spin in the system will reverse, and \( r \) is a homogeneous \([0,1]\) random number.

The transition probability \( W \) that a spin reverses from \( S \) to \(-S\) is assumed, which is analogous to the empirical theory, such that the chemical reaction is as follows:

\[
W = f \exp \left( -\frac{E_b}{k_B T} \right) \quad (E_i \geq E_f), \quad W = f \exp \left[ -\frac{E_b + E_i - E_f}{k_B T} \right] \quad (E_i < E_f),
\]

where \( E_b \) is an activation energy that generally exceeds an intermediate state, \( E_i \) and \( E_f \) are the initial and final energies in the transition, respectively. \( E_i \) for \( j \)-th spin is given by \( E_i = -J S \sum_k S_k n_k \), in which summation is taken over the nearest sites of \( j \) and \( n_k \) is the number operator for random configuration, 1 or 0. \( f \) is the attempt frequency for the transition, \( T \) is the temperature of the system, and \( k_B \) is the Boltzmann constant. Since the spin quantum number change is considered to include no intermediate state, \( E_b \) should be 0. Note that the change of the interaction energy in the process is taken into account through \( E_i \) and \( E_f \). The frequency \( f \) is assumed to be determined from the mean energy of the lattice vibration. At low temperature, \( f \) is obtained from

\[
hf = \frac{3 \pi^4}{5} k_B T \left( \frac{T}{\Theta_D} \right)^3,
\]

where \( \Theta_D \) is the Debye temperature of the material. The value of \( \Theta_D \) of the subject material Mn,Cd,(HCOO)\(_2\)-2(NH\(_2\))\(_2\)CO is 128 K.

The exchange interaction \( J \) can be determined to fit the Curie temperature of the pure system (\( x = 1 \)), \( T_c = 3.77 \) K, by the following equation (due to the exact solution of the 2-D Ising model):

\[
k_B T_c \approx 2.77 J.
\]

Then, the present simulation has no adjustable parameter.

3. Results of simulation
Calculations corresponding to the NMR spin echo experiment on Mn,Cd,(HCOO)\(_2\)-2(NH\(_2\))\(_2\)CO [1,2] were performed. The average \( i \)-site spin \( \langle S_i \rangle \) during time \( t \), \( \langle S_i \rangle_t \), is calculated for each spin. Figure 1 shows histograms of \( \langle S_i \rangle_t \) for the case in which \( x = 0.6 \) at \( T = 2.00 \) K. The horizontal axis shows \( \langle S_i \rangle_t \) with a resolution of 0.001, and the vertical axis shows the corresponding frequency. For the case in which the observation time \( t \) is short, \( \langle S_i \rangle_t \) is approximately 1 or -1, which indicates that the spins almost freeze, but as \( t \) increases, the peak around 0 grows larger, showing that the spins are become disordered with time. Figure 2 shows the histogram of \( \langle S_i \rangle_t \) for the case in which \( x = 0.9 \) at \( T = 3.40 \) K. A trend similar to that in Figure 1 is observed more clearly in Figure 2. In both cases, the states are paramagnetic at the considered temperatures, but the order parameters defined in NMR are finite values, especially for shorter observation times.

The observed order parameter in the NMR spin echo experiment is considered to correspond to the square root of the second power average of \( \langle S_i \rangle_t \) over all spins, as follows:

\[
\sqrt{\frac{1}{N} \sum_i \langle S_i \rangle_t^2} = \bar{S}_t.
\]
In Figure 3, the calculated results for $S_t$ are plotted for various observation times for $x = 0.6$. Since the concentration ($= 0.6$) is approximately equal to the percolation concentration ($\approx 0.593$), gradual phase transitions are expected to be most pronounced for this case. The calculated results exhibit quite gradual behavior, even for the longest observation time ($10^{-4}$ sec). For comparison, the calculated results for the case of the pure system ($x = 1$) are plotted in Figure 4. Even in the pure system, gradual transitions occur for shorter observation times, but the phase transition becomes sharper for the long observation time ($10^4$ sec).

Figure 1. Histograms of $\langle S_t \rangle_t$ for $x = 0.6$ at $T = 2.00$ K.

Figure 2. Histograms of $\langle S_t \rangle_t$ for $x = 0.9$ at $T = 3.40$ K.

Figure 3. Temperature dependence of order parameter $S_t$ corresponding to the spin echo experiment for $x = 0.6$.

Figure 4. Temperature dependence of order parameter $S_t$ corresponding to the spin echo experiment for $x = 1$.

Systematic experiments to examine the order parameter as a function of observation time have not yet been reported. In 2006, Kubo et al. measured the order parameter in a spin echo experiment for...
various observation times [2]. Figure 5 shows the proton NMR half-line width of the powder sample of Mn$_x$Cd$_{1-x}$(HCOO)$_2$·2(NH$_2$)$_2$CO obtained in the spin echo experiment. The half-line width of powder sample represents the order parameter $\bar{S}_t$ [2].

In the pure system ($x=1$), the phase transition occurs sharply and the order parameter varies only slightly between the different observation times (40 and 90 μs). On the other hand, for $x=0.89$, the order parameter varies noticeably between the different observation times (40 and 120 μs). Note that this difference does not appear at either lower or higher temperatures. The calculated results for the same conditions are shown in Figure 6. These figures reveal that the simulation reproduces well the characteristic features of the experiment. In detail, however, some discrepancies are present: for $x=0.89$, the transition temperature becomes larger than experimental one, and for $x=1$, a smaller but finite difference due to the observation time appears in the intermediate temperatures on the contrary to the experimental result. We consider that these disagreements are due to the simplification of the present model as explained in 2.1.

4. Summary and conclusion

In order to describe non-equilibrium phenomena of random magnetic systems, a time-dependent simulation scheme is proposed. This scheme is applied to explain the results of an experiment on the time-dependent order parameter of Mn$_x$Cd$_{1-x}$(HCOO)$_2$·2(NH$_2$)$_2$CO reported by Zenmyo et al. [1] and Kubo et al. [2]. The results of the present simulation reproduce well the characteristic features of the experiment. The proposed scheme of dynamic Monte Carlo simulation can be generally applied to time-dependent phenomena in magnetic systems.

References

[1] K. Zenmyo, H. Kubo, M. Tokita, K. Takeda, and K. Yamagata, J. Magn. Magn. Mater. 277 (2004) 281.
[2] H. Kubo, K. Zenmyo, T. Kato, and K. Yamagata, J. Magn. Magn. Mater. 310 (2007) e528-e530.
[3] Binder K, Monte Carlo Methods in Statistical Physics, Springer Berlin 1978, pp. 30-34.
[4] T. Kato, Y. Ohsawa, H. Kubo, and K. Zenmyo, J. Magn. Magn. Mater. 310 (2007) e531-e533.