New type of ordering process with volume change of molecules in the spin-crossover transition, and its new aspects of dynamical processes

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Abstract. Bistability between the high- and low-spin states in spin-crossover materials provides a complex temperature dependence of the ordering processes. Thermodynamic properties of the ordering phenomena were studied in a unified way, and a generic structure of the ordering processes was proposed. The origin of the interaction among the spins was also discussed, and a new mechanism based on an elastic interaction among distortions due to the volume of a molecule depending on its spin state was also proposed. With this mechanism, the typical pressure dependence of the ordering processes can be reproduced. Moreover, we studied the type of criticality of the phase transition and pointed out that the present model possesses critical behaviour belonging to the mean-field universality class. There, the spin-spin correlation function is constant at long distances and does not show an exponential decay in contrast to short-range models. It is also pointed out that the model with periodic boundary conditions does not show ordering clusters, even near the critical point or in the process of spinodal decomposition. This indicates that critical opalescence would not be observed in this model. No cluster appears, either in photo-excitation process from the low-spin state at low temperatures. On the other hand, with open boundary conditions, the system shows a cluster structure. The effects of the boundary conditions are also discussed.
1. Introduction

Bistability of the electro-vibrational state of certain molecules provides various interesting phenomena reflecting a competition between energy and entropy. For example, in spin-crossover materials, the competition between the crystal field and the degeneracy of the spin states plays an important role. Cooperative interaction among the molecules causes various types of change between the high-spin (HS) state and the low-spin (LS) state. Properties of the cooperative phenomena have been studied by introducing an Ising like model with a four-level model [1] and also a two-level model [2]. Recently, we found a metastable state of the high-spin state at low temperature which would be important to study the LIESTT (light induced excited spin state trapping) phenomena [3]. We also pointed out that, although there are many types of materials, e.g. spin-crossover and charge-transfer materials, etc., the mechanism of their ordering processes is essentially the same, and we have proposed a generic structure of the ordering processes [4,5]. The size difference between HS and LS causes an effective long-range interaction through the elastic lattice distortion [6]. We found that the pressure dependence of the ordering process also follows the generic structure by using this model with volume change [7]. Interesting characteristics of the temperature dependence of the volume have also been studied [8]. We also found that the critical properties of the model belong to the so-called mean-field universality class [9].

Besides the equilibrium transitions, in non-equilibrium processes due to photo-excitation we find various interesting properties. There, cooperative interactions cause a kind of threshold phenomena, and a phase-separation process in the photo-excited process was found [10]. We study such processes both in an ordinary short-range interacting model and also in the system with long-range interactions due to the elastic interaction among the distortions. The domain structure in the ordering process is a very interesting problem [11], and this problem has been studied in spin-crossover systems [9,12,13] as a hot topic.

2. General structure of ordering

We study a generic Hamiltonian of a spin-crossover type phase transition,

\[ H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j + (D - k_B T \ln g) \sum_i \sigma_i \]

where \( \sigma_i = \pm 1 \) denote the high- and low-spin states, respectively, \( D \) is the crystal field and \( g \) is the ratio of degeneracy of the high- and low-spin states (\( g > 1 \)) [2]. The first term is for the cooperative interaction. If \( D \) is large, the high-spin fraction \( q(T) \) shows a smooth change between the high- and low-spin states. When \( D \) becomes small, the system exhibits a first-order phase transition. If \( D \) is very small, the system stays in the high-spin state at all temperatures. For intermediate values of \( D \), we find a metastable branch of the high-spin state in a low-temperature region as depicted in Fig.1.

![Figure 1](image1.png)

**Figure 1.** Metastable branch at a low temperature.

The arrow denotes a photo-excitation process.

This branch preserves the photo-excited high-spin state for a long time. Even in the situation where the high-spin state is thermodynamically unstable, there exists an energy barrier between the high- and low-spin states in the energy structure of each molecule, as depicted in Fig.2 [9]. Therefore, the photo-excited high-spin state can be kept for a while in the unstable HS state. We may call the latter case...
“atomic metastability”, and the former “thermodynamic metastability”. It would be an interesting problem to distinguish the two cases in experiments.

In Fig. 2, we give the general phase diagram of the model, where the types of ordering I, II, III, IV, and V are schematically given on the right-hand side.

![Phase diagram](image1)

**Figure 2.** The general phase diagram of the types of temperature dependence of the ordering processes.

3. Elastic interaction and the mean-field universality class

Recently, we studied the origin of the interaction among the spins. In spin-crossover materials, the volume of a molecule changes, depending on whether it is in the HS or LS state (see Fig.3). This change causes distortion of the lattice, and the elastic interactions among these distortions can induce the generic structure of ordering patterns [6]. We also reproduced the typical pressure dependence of the ordering processes using a model of the elastic interactions [7].

![Intra-molecular potential and lattice distortion](image2)

**Figure 3.** Intra-molecular potential, and a lattice distortion due to the size difference of the high- and low-spin states.

Moreover, we studied the type of criticality of this phase transition. It was found that the critical behavior caused by this elastic interaction belongs to the mean-field universality class [9]. In this case, the critical exponents for the order parameter and the susceptibility are 1/2 and 1, respectively. The data were also expressed in terms of finite-size scaling plots. We found that the critical properties are well described by those of the infinite-range model (the Husimi-Temperley model), in which the total number of spins in the system (not its linear size) characterizes the finiteness. In this universality class, the spin-spin correlation function is constant at long distances, and it does not show an exponential decay in contrast to short-range models.

The model did not exhibit clusters of ordered states, even near the critical point. We also found that cluster growth was suppressed in a process of spinodal decomposition at the edge of the hysteresis loop, and we believe that there is no critical opalescence in the coexistence region. These curious properties are expected to be observable in experiments. We may understand the reason for the absence of large clusters from a viewpoint of elastic distortion. If a large cluster exists, it causes a large deformation of the lattice, which is not favorable for the elastic interaction, and the system tends
to avoid such configurations. In Fig. 4(a), we show a comparison of configurations with large domains in the cases with and without a size difference between the high- and low-spin states. The left is a typical spin configuration of the Ising model with short-range interactions near the critical point, where we find a large cluster structure. If we take into account the size difference between the HS and LS states and relax the lattice structure, we have the configuration on the right.

Signs of clustering have been observed in experiments [10]. We have to investigate how clusters can exist in volume-changing materials. The coexistence of long-range and short-range interactions would cause a domain structure that has a characteristic length [11,12], which is an interesting problem. Here we would like point out the problem of the boundary conditions. So far, we have usually adopted systems with periodic boundary conditions. In a quenching process in a system with open boundary conditions, the appearance of a cluster structure has been pointed out [13]. In our model, a cluster structure also appears in quenching process with open boundary conditions, as depicted in Fig. 4(b). The boundary conditions have significant effects in the model with effective long range-interactions. We therefore have to consider seriously the effects of the boundary conditions in experiments.

![Figure 4](image)

**Figure 4.** (a) Comparison of the configurations with and without size differences. (b) Clustering structure which appears in a quenching process with open boundary conditions.

4. Threshold phenomena in photo-excited processes

We also study the ordering properties under photo-irradiation. In particular, we study the threshold phenomena due to cooperative effects. The photo-excitation process in each molecule can be expressed by Fig. 5. There, we adopt a coupled local system. It is characterized by a set of combined rate equations for the populations of the states: HS, LS, and excited state A and B (given in Fig. 5). There, $a$ denotes the strength of the photo-excitation, and other parameters denote other processes. We simulated a system consisting of such local systems with short-range interactions, and found a threshold behavior of $a$ at which the saturated high-spin density jumps significantly.

![Figure 5](image)

**Figure 5.** Photo-excitation process in a molecule. (b) A typical excitation process of the high-spin fraction in the elastic model with periodic boundary conditions.
The system also shows a kind of dead time during the irradiation, i.e., the system stays in the low-spin state for a while before it jumps suddenly to the high-spin state. In this way, we find a threshold phenomenon as a function of time, in line with mean-field expectations [14]. These threshold phenomena are a characteristic of interacting systems. In the short-range interaction system, we find a clustering structure during the transition as naturally expected.

We also studied the photo-excitation effects in systems with elastic interactions. There, we found threshold phenomena as well. However, we do not find a domain structure as shown in Fig. 6. This domain-less excitation process is a new characteristic of the elastic model. Moreover, the size dependence of the relaxation time \( \tau(L, a) \) is found to diverge at the threshold value of \( a \), which is again a characteristic property of the mean-field model. These properties due to the effective long-range interactions represent a new feature of cooperative phenomena, and we expect that they will be found in related experiments.

Figure 6. Time evolution of the HS fraction under the photo-irradiation process, and spin configurations during the process.

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