Modeling of Nano-Structure via a Spinodal Decomposition: An Extended Range of Monte Carlo Investigation

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ABSTRACT

In the study, we proposed a Monte Carlo package to investigate the spinodal decomposition which is a pathway to obtain nano-structure phase of materials. The modeled system consists of two different species of the Ising spins where the order parameter is conserved. The interaction range among atoms, being assumed to take an inverse square law behavior, was extended to the third nearest-neighbor range, i.e., two times the lattice spacing. A separate simulation on only the first nearest-neighbor range was also taken for a comparison. The growth of the mixing and de-mixing of the Ising spins was observed in terms of the nucleation growth of similar atoms via the correlation length. From our results, the nano-stripe pattern of spinodal decomposition was evident. The power law relation between the spinodal domain size and the simulation time was found for both the first and the third nearest-neighbor interaction range. However, the exponent to the growth rate of the third nearest-neighbor interaction system is slightly smaller than that of the first nearest-neighbor interaction system, suggesting a slower growth in time. This proposes that the growth exponent is sensitive to the interaction range, and an appropriate interaction range must be used to model spinodal decomposition in real materials.

Key words: Nanostructure, Spinodal decomposition, Monte Carlo, Ising model, Kawasaki algorithm

INTRODUCTION

Recent advances in the physical science and engineering have been focused on expanding the limits of our understanding of material behaviour to ever-shrinking-length scales, using a complimentary array of atomic-scale modeling techniques and sub-nanometer scale characterization methods. These efforts have resulted in numerous successes, most notably including the advent of nano-materials which impacts numerous facets of our society. Within the broad spectrum of nano-materials, a wide range of technological capabilities exist which draw upon the unique characteristics of the behaviour of materials at the nanoscale. These include novel chemical and biological sensors (Tu and Chen, 2002), nanoscale microprocessors (Plouchart, 2003), photonic crystals (Leung et al., 2003), nano-electromechanical systems (NEMS) (Tang, 2001), and many others. One of the most critical aspects of designing nano-scale devices is the ability to manipulate or assemble materials at the nanoscale. Numerous approaches have been attempted with various degrees of success. Even in single-phase systems, it is difficult to preserve a nano-crystalline structure because of the strong driving forces for grain growth which lowers the energy of the system by reducing surface or grain-boundary energy. Therefore to synthesize bulk nano-crystalline metals or ceramics, it is often necessary to use non-equilibrium process conditions to preserve the nano-crystalline

state. The ideal method for fabricating this structure would rely on known thermodynamic driving forces such that the characteristics of the nanostructure can be controlled under experimentation. It is proposed that the well-known phenomenon of spinodal decomposition is uniquely suited to this purpose where nanostructure can be reproducibly controlled though experimental parameters such as temperature, time and doping.

The spinodal decomposition is a mechanism for phase separation which leads to a characteristic modulated structure which can be exploited to control the microstructure at the nanometer scale. Being known from the dynamics of the growth in an unstable state, the spinodal decomposition is formed when a system is rapidly quenched from a high-temperature disordered state to a temperature below its critical temperature T_C. Interestingly, this spinodal decomposition is of a major concern in modern thin-film and nanostructure technologies due to the allowance of two or more separate nano-scale phases to coexist in a system. As a result, the control of the spinodal decomposition is very vital in terms of fundamental and technological importance, e.g., a pathway to obtain nano-sized lamellae to maximize the efficiency in ceramics processing (Chaisan et al., 2005) and the growth of nanocrystalline structure which can be used to control the hardness of materials (Hörling et al., 2005). Consequently, an extensive understanding of the spinodal decomposition phenomenon is very crucial if one wants to apply the nano-technology to the innovative industrial applications.

However, for simplicity, many theoretical studies of the spinodal decomposition phenomenon have been performed in the simplest case, e.g., only the nearest-neighbor interaction is taken into account, or a system with a longer interaction range is considered but the coupled interactions are of a same magnitude (Herrmann et al., 1982). As a result, this may simplify the problem into an optimum level but, in turn, may lead to incorrect results if the longer-range interaction is not small in comparison with the nearest interaction. For instance, in the case of electro-materials, the interaction is a function of the distance where the electronic interaction ceases with the inverse square law. Because of this, there comes the objective of this study. We tried to understand the effect of the longer-range interaction (up to the third nearest-neighbor) on the spinodal behavior.

To outline, we studied the growth of nano-stripe pattern via the spinodal decomposition with the exchange interaction ranging from the first to the third nearest-neighbor, using Monte Carlo simulations. The considered system consisted of two-mixable Ising species (binary alloy like-wise), located only on square lattice grids, being influenced by the inverse distance-square coupling interaction at a temperature below the critical temperature T_C. The configuration update-algorithm being used was the Kawasaki algorithm (Kawasaki, 1966), allowing the exchange of the atoms between those two species but the number of each kind was conserved macroscopically. The observables were taken in terms of the domain size as a function of temperature and the simulation time. The domain size of the spinodal decomposition was extracted from where the order parameter correlation function arrives at its first zero crossing. Then, the results were analyzed under the framework of nucleation growth and discussed in details.

MATERIALS AND METHODS

In the study of the out-of-equilibrium relaxation phenomenon in the spinodal decomposition, we considered the mixing and de-mixing processes, corresponding to an evolution of a solid AB binary alloy. The de-mixing process is categorized in terms of the growth of ordered domains which the system tends to form a cluster of similar atoms (species). On the other hand, the mixing process, being inspired by the thermodynamic diffusion, tends to

distribute the two species into any sub-space of the system with an equal probability. Consequently, this forms a mixing state of a solid solution-like pattern. However, as mentioned earlier, when the system is quenched from a high-temperature disordered phase to a temperature below critical temperature, the spinodal decomposition phase is formed by the process of mixing and de-mixing. Groups of similar atom clusters will start to grow which is, in general, a function of time following the power law:

$$r(t) \sim t^n \tag{1}$$

where r is the averaged domain size , t is the annealing time and n is the growth exponent. From the Lifshiftz-Slyozov law (Lifshitz and Slyozov, 1961), the exponent was predicted 1/3 for the conserved order parameter system (a system that the total of number of atoms in each species is fixed). This value is independent of the dimensionality *d* and is considered to be universal. However, since the Lifshiftz-Slyozov law was proposed from the diffusion equation, any movement of the domain walls between two different phases that disobey the one-lattice-spacing exchange will not take $n = 1/3$. For example, in the binary system where there is an inclusion of vacancies, the exchange between the occupied sites and vacancies suggest $n > 1/2$ (Vives and Planes, 1992) and this value decreases towards the value 1/2 for temperatures approaching the critical ordering temperature due to fluctuations.

In our Monte Carlo simulation, the mixing and de-mixing process are caused by the trial exchanges of atoms of the two species at the particular temperature T. The concentration of the two species was fixed at 0.5 and the total number of atoms in the system was $N = L$xL = 200x200 atoms (20000 A atoms and 20000 B atoms). The interaction among the atoms was modeled by using an Ising Hamiltonian:

$$H = -\sum_{ij} J_{ij} S_i S_j \tag{2}$$

where $S_i = \pm 1$, referring to the A and B species, resides only on rigid square lattices. Unlike previous studies, the sum in Eq. (2) takes beyond the nearest-neighbor pairs to the third nearest- neighbour pairs and $J_{ij} > 0$ is the interaction energy between site i and j. As a result, we can rewrite Eq. (2) as:

$$H = -\sum_{1nn} J_{1nn} S_i S_j - \sum_{2nn} J_{2nn} S_i S_j - \sum_{3nn} J_{3nn} S_i S_j \tag{3}$$

where J_{1nn}, J_{2nn}, and J_{3nn} refer to the first nearest-neighbor, the second nearest-neighbor and the third nearest-neighbor exchange interaction respectively. Due to an assumption of inverse square law form, on a square lattice, $J_{2nn}/J_{1nn} = 1/2$ and $J_{3nn}/J_{1nn} = 1/4$. During the simulation, we used J_{1nn} as a unit of energy. Therefore, this redefines the unit of temperature T to J_{1nn}/k_B. For the simulation update, we considered the use of Kawasaki algorithm and such a case that n 1/3 may happen. This is due to that, in stead of allowing only the adjacent atom to get exchanged, we allowed a ballistic-like exchange. For example, we made a list of A atom and B atom. Then, we randomly picked up both an A atom from the A list and a B atom from the B list. After that, we proposed that exchange between these 2 atoms with a probability:

$$P = \exp\left[-\frac{H}{k_B T} \right] \tag{4}$$

where k_B is Boltzamann's constant, and H is the energy difference between the before-exchange and after-exchange states. For a lattice with N sites, the time-unit is defined in terms of 1 Monte Carlo step (mcs) which is N trials of atom-atom exchanges.

In selecting the simulated temperatures, we considered the temperature below but close to the critical temperature (the phase-transition temperature between the ordered and the disordered phase). For the system with only the first nearest-neighbor pair (1nn system), we chose $T = 2.04\ J_{1nn}/k_B$ and for the exchange interaction up to the third nearest-neighbor pair (3nn system), we chose $T = 4.00\ J_{1nn}/k_B$. The initial configurations for both the 1nn and 3nn systems were the disordered state where A atoms and B atoms randomly mixed throughout the lattice. The size of the domain growth in the spinodal decomposition was extracted from the order parameter correlation function $g(r,t)$ which for the Ising model is

$$g(r,t) = \{S(0,t)S(r,t)\} - \{S\}^2 \qquad (5)$$

where r is the spatial distance in a unit of lattice spacing. Then the averaged domain size r_0 was taken from the first distance r that brought the correlation function to zero. For each simulation, the correlation function were recorded as a function of time t which the longest time was taken up to 10^5 mcs. To minimize the systematic and statistical errors, we repeated the procedure for each system and obtained results from 100 independent runs. The correlation functions were calculated for each run and the average correlation are averaged from these 100 runs to extract the domain size r_0.

RESULTS AND DISCUSSION

From the simulations, we obtained the kinetic ordering-disordering profiles caused by the mixing and de-mixing process. Figures 1 and 2, which are the snap shots of configurations of the 2 species during the annealing processes, present such a case.

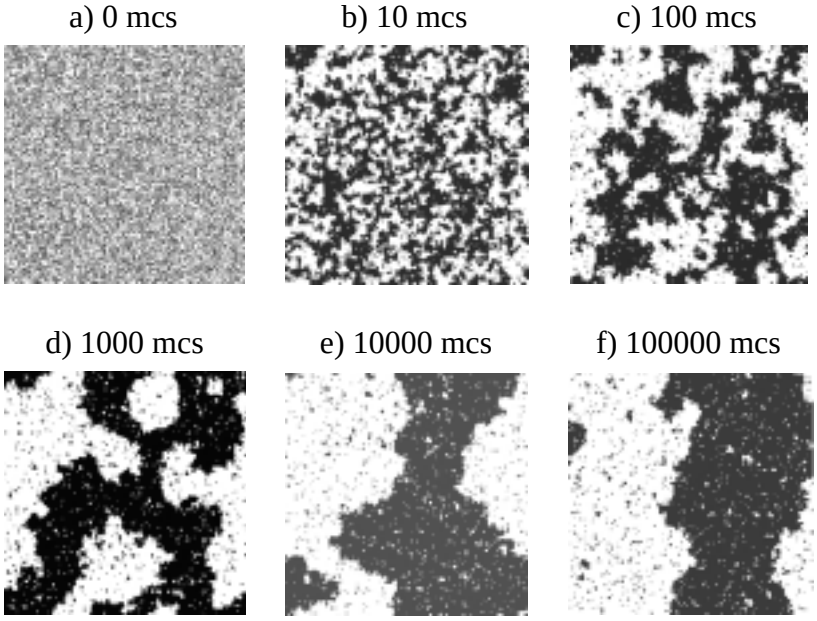

Figure 1. Snap shots of configurations at 0, 10 , 100, 1000, 10000 and 100000 mcs's simulated with only J_{1nn} at $T = 2.04\ J/k_B$. Black and white dots refer to different species of the binary system.

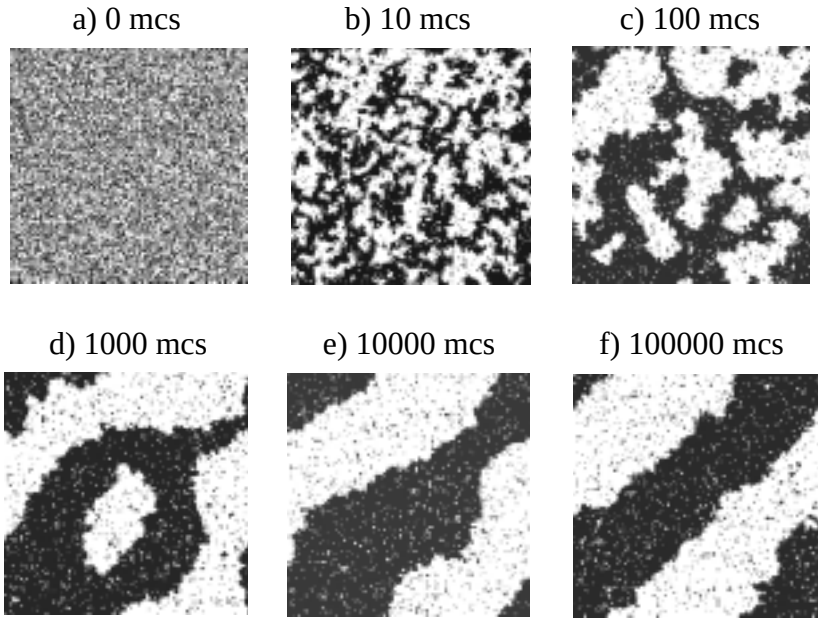

Figure 2. Snap shots of configurations at 0, 10 , 100, 1000, 10000 and 100000 mcs's simulated in a system with exchange interactions up to 3nn at $T = 4.00\ J/k_B$. Black and white dots refer to different species of the binary system.

From the figures, it is clear that the competition between the mixing and de-mixing process determines the configurations of spinodal decomposition. With a sudden quench from a temperature above the critical temperature, the group of similar atoms tends to form. Starting with stripes, the cluster gets growing as the annealing time (simulation time) goes by. This is due to that the system tries to lower down its internal energy by reducing the domain surface [see Eq. (3)]. Therefore, the system updates itself in such a way of moving similar atoms to stay close to their kind. In comparison between system with only 1nn exchange interaction (1nn system) and system with the exchange interaction up to 3nn (3nn system), it is clear that the cluster in the 3nn system has a bigger size on a same time scale. This is expected since the exchange interaction coupling in the 3nn system is stronger. Hence, unsatisfied pair (a pair between dislike atoms) will not be likely to occur, and this results in that a cluster of like-atoms becomes bigger at a same time scale. Figure 3, which displays the normalized correlation function $g(r,t)/g(0,t)$ as a function of spatial distance, shows such evidence.

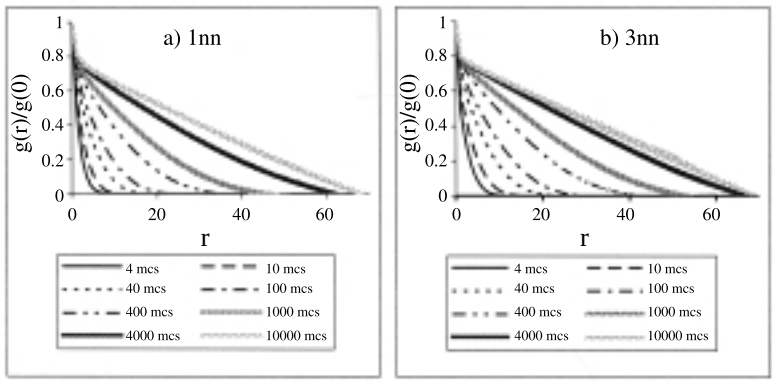

Figure 3. The normalized correlation functions of the systems (a) with 1nn exchange interaction only at $T = 2.04\ J/k_B$ and (b) with interaction-range extending to 3nn at $T = 4.00\ J/k_B$ as a function of the spatial distance r.

As can be seen from the figure, at a same duration of time, the correlation function for the 3nn system [Figure (3b)] arrives at zero with an averaged domain size r_0, bigger than that of the 1nn system [Figure (3a)]. However, since the cluster in the 3nn system is already very big at the early state of annealing, the cluster size should not be far from its saturated level. Therefore, the exponent nucleation growth rate n in Eq. (1) for the 3nn system should be smaller that that of the 1nn system. Following Eq. (1), the extraction of the growth exponent n from the log-log plot of the averaged domain size and the annealing time supports this [see Figure 4].

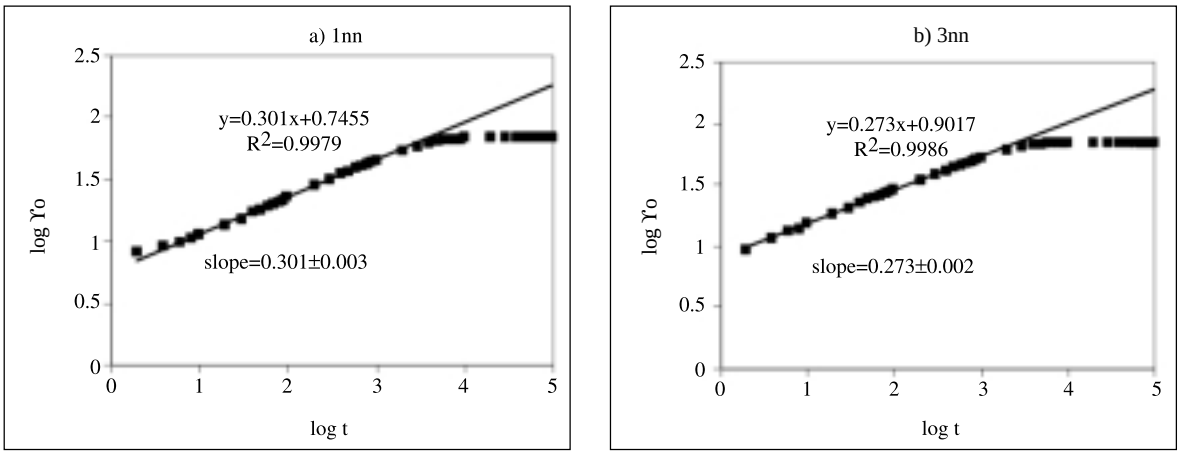

Figure 4. The double logarithmic plot of the average domain size (log Υo) and annealing time (log t) for (a) system with only 1nn exchange interaction at $T = 2.04\ J_{1nn}/k_B$ and (b) systems with exchange interaction-range extending to 3nn at $T = 4.00\ J_{1nn}/k_B$. The straight lines are the best linear fits to the results in the region that linear-relationships are present.

In Figure 4, the least square linear-fits are taken on the region where the linear-relationship is found. It should be noted that the late annealing stage (close to 10^5 mcs), those domain sizes should not be included in the fit since the finite size effect becomes important and puts some constraints on the domain growth. Also in the figure, the 1nn system has the growth exponent $n = 0.301 \pm 0.003$ which is bigger than that for the 3nn system which has $n = 0.273 \pm 0.002$ as expected. As can be seen, this slight difference suggests that growth exponent is sensitive to the interaction range.

CONCLUSION

In this study, we investigated the effect of an extended range interaction of the exchange coupling in a form of an inverse square law on the nucleation growth in the spinodal decomposition process. From the result, the nano-stripe pattern of the spinodal decomposition appears in both the 1nn and 3nn systems. The power law relation between the averaged domain size and the annealing time from both interaction ranges (1nn and 3nn) is also evident. However, the extended range 3nn system seems to have a bigger cluster size at a same time scale. On the other hand, to pay its cost, the nucleation growth rate in the 3nn system drops a little since it has already come closer to its saturated state. To conclude, the study suggests the success in modeling nano-structure via spinodal decomposition by using Monte Carlo technique which can extend the understanding and predict the mechanism of phase separation under the effect of long-ranged interaction.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Faculty of Science, Chiang Mai University and the Thailand Research Fund (TRF) for financial supports.

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