

Kinetics of Order-Disorder Transitions in Binary Mixtures: A Monte Carlo Study

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Abstract. We study ordering kinetics in symmetric and asymmetric binary mixtures, undergoing an order-disorder transition below the critical temperature. We model the microscopic dynamics via an anti-ferromagnetic Ising model with Kawasaki spin-exchange kinetics. This conserves the composition but the order parameter, (staggered magnetization) is not a conserved quantity. The order-parameter correlation function shows dynamical scaling, and the scaling function is independent of mixture composition. The average domain size exhibits power law growth: $L(t) \sim t^\alpha$. The asymptotic growth regime has $\alpha = 1/2$, though there can be prolonged transients with $\alpha < 1/2$ for asymmetric mixtures. Our unambiguous observation of the asymptotic universal regime is facilitated by use of an accelerated Monte Carlo technique.

1. Introduction

Phase ordering processes are of great interest in the fields of material science and metallurgy for the designing of new materials [1, 2, 3]. When a disordered binary mixture A_xB_{1-x} is suddenly quenched below the order-disorder critical temperature, $T_c(x)$, the system evolves toward two degenerate (ABAB and BABA) ordered domains. The mixture is said to be symmetric if $x = 0.50$, otherwise asymmetric, for ordering in bipartite lattices [4, 5]. The kinetics of order-disorder transitions in symmetric mixtures is well-studied by using microscopic and coarse-grained models [6, 7]. At the microscopic level, the order-disorder transition is investigated using the nearest-neighbour (n.n) Ising anti-ferromagnet with Kawasaki spin-exchange kinetics. The average domain size $L(t)$ grows with time as $L(t) \sim t^{1/2}$, corresponding to diffusive growth with non-conserved order parameter (Cahn-Allen theory) [8]. The driving force of this growth process is the local curvature of the interfaces between differently-ordered domains. The domain morphology is studied using the order-parameter correlation function $C(r, t)$, and structure factor $S(k, t)$. These quantities show dynamical scaling with the scaling forms:

$$C(r, t) = g(r/L), \quad (1)$$

$$S(k, t) = L^d f(kL), \quad (2)$$

where d is the spatial dimensionality. Here, $g(x)$ and $f(p)$ are master functions, which are independent of time.

The kinetics of ordering has been studied experimentally for both symmetric and asymmetric compositions [9, 10]. For symmetric mixtures, the average domain size grows very slowly at the



early stages, with a crossover to the $t^{1/2}$ -law at late times [9]. The first experimental study of ordering kinetics in asymmetric mixtures is due to Shannon *et al.* [11]. They studied ordering kinetics in sputtered films of $\text{Cu}_{0.75+x}\text{Au}_{0.25-x}$, which has *fcc* structure. Below T_c , for symmetric compositions with $x = 0.00$, domain coarsening is consistent with $t^{1/2}$ -law. The domain growth in asymmetric films with $x = 0.04$ is much slower, and shows logarithmic time dependence. The “logarithmic” regime could be a consequence of quenched impurities [12, 13]. It is also possible that it could be a transient regime prior to an asymptotic power law growth.

The first theoretical study of phase ordering in asymmetric binary mixtures is due to Porta *et al.* [14], using the n.n anti-ferromagnetic Ising model with Kawasaki spin exchange dynamics. They studied the effect of composition asymmetry on phase ordering in A_xB_{1-x} mixture, with $x \leq 0.50$ in two dimensional square lattices. The characteristic length scale of domain growth follows power law $L(t) \sim t^\alpha$, with exponent $\alpha \sim 0.40 - 0.50$ for x lying in the range 0.40 to 0.50. However, they predicted the growth law $L(t) \sim t^{1/2}$, irrespective of the asymmetry. First principle study of Sanati and Zunger [15] also confirms the above growth law in the late stage of ordering in *fcc* Cu_3Au alloys. In this paper, we numerically study the kinetics of order-disorder transitions in A_xB_{1-x} mixture. For asymmetric mixtures, there is lack of clarity regarding the asymptotic growth regime due to slow transients. We use an accelerated Monte Carlo (MC) algorithm to unambiguously demonstrate the following:

- (i) The asymptotic domain growth law is $L(t) \sim t^{1/2}$, regardless of the composition of the mixture.
- (ii) The scaling functions, which characterize the evolution morphologies, are universal for different values of x .

This paper is organised as follows. In Sec. 2, we describe our numerical techniques including the accelerated MC algorithm. In Sec. 3, we present detailed numerical results. Finally in Sec. 4, we conclude with a brief summary and discussion.

2. Details of Numerical Simulations

For the microscopic model, we start with the Ising model Hamiltonian:

$$\mathcal{H} = J \sum_{\langle ij \rangle} S_i S_j. \quad (3)$$

In Eq. (3), J is the strength of exchange interaction and is positive for order-disorder transition. The subscript $\langle ij \rangle$ represents n.n interaction and $S_i = +1$ or -1 corresponds to A or B atoms of the binary mixture respectively. We study ordering dynamics of our model given by Eq. (3) with Kawasaki spin exchange kinetics in $d = 2$ [1, 2]. This microscopic kinetics individually conserves numbers of $S_i = \pm 1$. The system size is N^2 with $N = 4096$. We employ periodic boundary conditions in all the directions.

The initial condition of our MC simulation consists of random distribution of A and B with number densities $c_B = 1 - c_A$, mimicking the disordered state before the quench. At $t = 0$, the system was quenched below $T < T_c$, the A and B atoms order on alternate sublattices of the square lattice. The appropriate order parameter is *staggered magnetization* M , which is the difference between two sublattice *magnetizations* of square lattices. It is not conserved under the Kawasaki kinetics and is equivalent to the ferromagnetic Ising model ($J < 0$) with Glauber kinetics [1, 2]. A randomly chosen pair of unlike spins have interchanged according to the above stochastic move, corresponding to a change in configuration from $\{S_i\} \rightarrow \{S'_i\}$. The change is accepted with the probability p , given by

$$p = \begin{cases} 1 & : \Delta E \leq 0 \\ \exp(-\beta \Delta E) & : \Delta E > 0 \end{cases} \quad (4)$$

where $\Delta E = \mathcal{H}(\{S'_i\}) - \mathcal{H}(\{S_i\})$ is the energy difference between the final and initial configurations and $\beta = (k_B T)^{-1}$ with $k_B = 1$. Here one Monte Carlo Step (MCS) corresponds to N^2 attempted updates. All the statistical results presented here are obtained as averages over ten independent runs.

In the accelerated approach, we use the algorithm proposed by Marko and Barkema (MB) for phase-separating binary alloys [16]. The MB algorithm accelerates to reach asymptotic growth law by suppressing diffusion along the interfaces and favouring interdomain bulk diffusion. This is because, in the late stage of evolution, a small fraction of time is spent on intradomain transport processes, which generate actual growth law and dynamical scaling. Here, we modify the MB algorithm for the order-disorder transitions. In the modified approach, we keep track of the coordination number of each site i ,

$$Q(i) = \sum_{j \in \langle i, j \rangle} \delta(S_i, -S_j). \quad (5)$$

The $Q(i)$'s run from 0 to Z , where Z is the lattice coordination number. Here, $Z = 4$ in two dimensional square lattices. Isolated spins i whose neighbours are same in sign have $Q(i) = 0$, while spins i , whose neighbours have opposite sign have $Q(i) = Z$. The coordination numbers provide sufficient information to compute energy changes due to spin exchanges. The change in energy resulting from the exchange of two nearest neighbour spins i and j of opposite sign is given by

$$\Delta E = 4J [Q(i) + Q(j) - (Z + 1)]. \quad (6)$$

We order all the sites having equal coordination number into lists. Thus, we have $Z + 1$ lists and all the sites in a given list have the identical environment. When the system quenches below T_c , ordering starts throughout the system. As a result, the size of the list with $Q(i) = Z$ will be increasing by shrinking size of the lists with $Q(i) < Z$. The steps of the algorithm are same as those proposed by MB [16]. However for the sake of completeness, we will mention the steps. We choose a step from the ensemble of all possible spin exchanges according to how likely it is to occur per unit time, making time step of appropriate duration. One step of our dynamics for a cubic lattice consists of the following parts:

- (i) to increment time by

$$\Delta t = \left[\sum_q \left(1 - \frac{q}{Z}\right) N_q e^{-4Jq} \right]^{-1}, \quad (7)$$

where N_q is the number of elements in the list with q neighbours. We call this time as *Monte Carlo time* (MCT).

- (ii) to select the list of q neighbours with probability

$$P_q = \Delta t \left(1 - \frac{q}{Z}\right) N_q e^{-4Jq}. \quad (8)$$

- (iii) to randomly select a site i from the list of q neighbours.
- (iv) to randomly select a neighbour j of site i with $S_i \neq S_j$.
- (v) to exchange the spins S_i and S_j according to the probability given by Eq.(4). Adjust Q values of the sites i, j and their neighbours and update the lists.

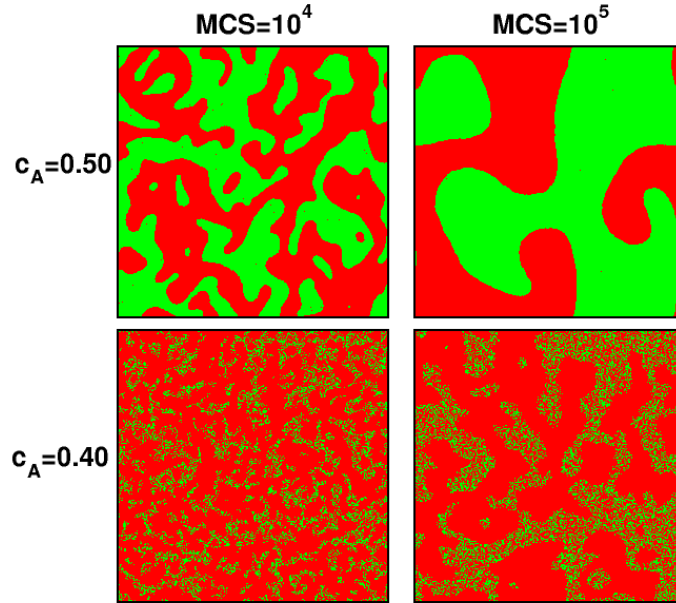


Figure 1. Evolution snapshots of staggered magnetization M , which is the magnetization difference between two sublattices, obtained from $d = 2$ MC simulations of Ising model described by Eq. (3). First row represents the same for mixtures with $c_A = 0.50$ and second row for $c_A = 0.40$ at two different MCS, as mentioned. The lattice size was 4096^2 and periodic boundary conditions were applied in both the directions. The initial condition for each run consisted of random mixtures of A and B, according to the desired ratio. The quenching temperature was $T = 0.9$ for both the cases. Regions with $M > 0$ are marked in red and that of with $M < 0$ are marked by green. From the evolution snapshots of the mixtures with $c_A = 0.40$, it is clear that the excess B-atoms (number of B-atoms, which is greater than A-atoms) were dissolved into the bulk.

3. Numerical Results

In Fig. 1, we show the evolution snapshots of the staggered magnetization field for $c_A = 0.50$ and $c_A = 0.40$ at different MCS, as mentioned. Details are given in the figure caption. For the symmetric mixture with $c_A = c_B = 0.50$, immediately after the quench below T_c , the system evolves toward two degenerate ABAB and BABA ordered states. At the late stage, the domain growth is driven by the removal of the interfaces between two differently ordered domains. But for asymmetric mixture with $c_A = 0.40$, ordering starts throughout the system and the excess B atoms start accumulating along the interface of the ordered regions immediately after quench below T_c . At the late stage of the domain growth, the excess B atoms start migrating into the bulk of the ordered domains by minimizing the energy. It is evident from the evolution snapshots for $c_A = 0.40$ in Fig. 1. For all other asymmetric compositions, similar dynamics is observed.

In order to study the morphology of domain growth, we calculate the correlation function and structure factor of the staggered magnetization field, defined as $\sigma_{ij} = (-1)^{(i+j)} S_{ij}$ for a spin S_{ij} at the site (i, j) in two dimensions. The equal time correlation function $C(\vec{r}, t)$ is defined as follows

$$C(\vec{r}, t) = \left[\left\langle \sigma(\vec{R}, t) \sigma(\vec{R} + \vec{r}, t) \right\rangle - \langle \sigma(\vec{r}, t) \rangle \langle \sigma(\vec{R} + \vec{r}, t) \rangle \right]. \quad (9)$$

Here the angular brackets represent the average over different initial conditions [18, 20]. Similarly, we calculate *structure factor* $S(k, t)$, which is defined as the Fourier transform of

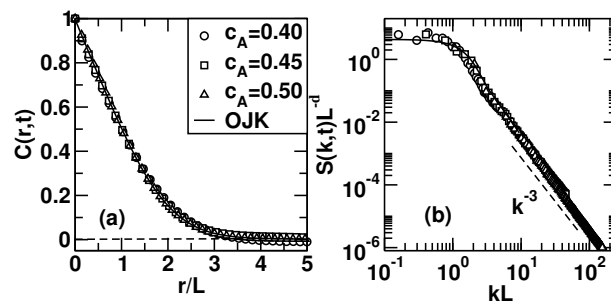


Figure 2. Scaling plot of spherically averaged correlation functions $C(r,t)$ and structure factors $S(k,t)$ of $\sigma(\vec{r},t)$ -field at MCS=10⁵ for different concentration of A. The system size is $L_x \times L_y = 4096 \times 4096$. Results are averaged over ten independent runs. (a) Plot of $C(r,t)$ at MCS=10⁵ for different c_A , as mentioned. We define the length scale L , which is the distance at which $C(r,t)$ falls to half from its maximum (=1 at $r=0.0$). The solid line shows the OJK function in Eq. (11), collapsed appropriately. (b) Plot of $S(k,t)$ vs. kL on log-log scale. The solid line denotes the Fourier transform of OJK function, scaled appropriately. The line labeled with k^{-3} represents the Porod's law with $d = 2$ and $n = 1$. Rest of the details are same as Fig.1.

the correlation function $C(r,t)$ as follows

$$S(\vec{k}, t) = \int d\vec{r} e^{i\vec{k} \cdot \vec{r}} C(\vec{r}, t), \quad (10)$$

at wave vector $\vec{k}$. The correlation function for the ordering in 50%-50% mixture is well studied and solved by Ohta *et al.* (OJK), who showed that length scale grows as $L_\sigma(t) \sim t^{1/2}$ [19]. The functional form of the correlation function is

$$C_{OJK}(r, t) = \frac{2}{\pi} \sin^{-1} \left(e^{-r^2/L_\sigma^2} \right). \quad (11)$$

In Fig. 2(a), we plot $C(r,t)$ vs. r/L at MCS=10⁵ for different values of c_A , as mentioned. We also plot the OJK function in Eq. (11). We see that numerical data for all values of c_A are indistinguishable from the OJK function, which confirms that the morphology of ordering in symmetric and asymmetric binary mixtures is same. In Fig. 2(b), we plot $S(k,t)L^{-d}$ vs. kL at MCS=10⁵ for different values of c_A , mentioned. We also plot the Fourier transform of the OJK function - this also matches with our numerical data. The data collapse confirms the dynamical scaling. In the limit $k \rightarrow \infty$, $S(k,t)$ decays as k^{-3} , following the *Porod's law* as $S(k,t) \sim k^{-(d+n)}$ with spatial dimensionality $d = 2$ and the number of order parameter components $n = 1$ [17]. This implies sharp interfaces formed between two degenerate ordered states, irrespective of the amount of surplus materials present in the system.

We calculate the length scale of domain growth L from the equal-time correlation function of the staggered magnetization field, as described earlier for regular MC. It is defined as the distance at which correlation decays from 1(at $r = 0$) to 0.5. The variation of average domain size L vs. MCT for different c_A 's are shown in Fig. 3. Details are given in the figure caption. Line with growth exponent $\alpha = 1/2$ in Fig. 3, corresponds to diffusive growth for non-conserved order parameter. Here the growth exponent is $\alpha = 1/2$ for all the mixtures. This is the well-known *Allen-Cahn Law*: $L(t) \sim t^{1/2}$ [8]. Asymmetric mixtures have less surface tension than symmetric ones. This is because of the saturation value of the order-parameter is less in the bulk of a ordered domain. This can give rise to slow transients. In Fig. 3, the $L(t)$ for $c_A = 0.50$ is smaller than that of for $c_A < 0.50$. This is because we quenched the systems for different c_A 's at same temperature and there is conversion factor between MCT and MCS, which is less for asymmetric mixtures than the symmetric mixture.

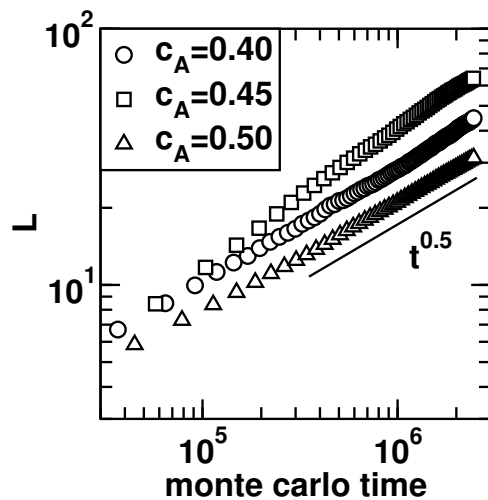


Figure 3. Time-dependence of the characteristic length scales L of M -field for various concentration of A component obtained from accelerated MC simulation. The system size is 2048^2 and quench temperature $T = 0.9$ for all the mixtures. Solid line with exponent $\frac{1}{2}$ is shown, corresponds to growth due to the diffusion process. Clearly, the growth exponent is same irrespective of asymmetry in compositions.

4. Conclusion

Let us conclude this paper with the summary and discussion of our results. We carried out phase ordering kinetics for symmetric and asymmetric binary mixtures via antiferromagnetic Ising model with Kawasaki spin-exchange dynamics. The equal-time correlation functions of staggered magnetization field for symmetric and asymmetric composition show data collapse, indicating the morphological similarity of domain growth. In the limit $k \rightarrow \infty$, structure factor tails decay as k^{-3} for both symmetric and asymmetric mixtures, implying sharp interfaces formed between two degenerate phase of staggered magnetization field irrespective of the composition. The universal domain growth law: $L \sim t^{1/2}$ for order-disorder transition in symmetric and asymmetric mixtures is obtained from accelerated MC algorithm. These results confirm the universality in the ordering of symmetric and asymmetric binary mixtures.

5. References

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