



## Path of ordering under confinement in alloy films

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### ABSTRACT

The effects of surface confinement on the kinetics of ordering in fcc alloy films are studied by the Monte Carlo method. Under weak surface confinement, there are two kinds of kinetic path for alloy films with even layer. One is the films directly relaxing to the equilibrium state, the other is the films relaxing to a metastable state first. Even for the same initial atomic configuration, the kinetic path of ordering is randomized, and the possibility that the films relax to a metastable state is independent with the initial atomic configurations. We attribute this randomness to the competition between surface confinement and chemical ordering. The evolution of the metastable state to the equilibrium state is also simulated. The results indicate that an alloy film with weak surface segregation can easily be trapped into metastable state.

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### 1. Introduction

Confinement and finite size effect can result in a number of phenomena different with those of the corresponding bulk structures. The structures and phase transitions of thin films are influenced by the confinement and finite size effects [1–5]. The growth of thin films with mono atomic layer accuracy can be achieved by various epitaxial growth methods for the control of film thickness. The two surfaces of thin films, which are contacted with vacuum or substrate, are considered as under two different surface confining (SC) field. The SC field leads to a diversity of phenomena of surface ordering [6]. In bcc alloy thin films with ordering interaction, the large SC field describing surface segregation can result in an unusual phase diagram with a disordered phase lying between the ordered phases down to zero temperature [7]. The order–disorder transition temperature of alloy films is significantly different from that of the corresponding bulk structure, due to the SC field and the finite size of films [8,9]. For the fcc binary alloys such as Cu<sub>3</sub>Au, experiments exhibit that there is surface induced disordering due to the SC field [10]. The perpendicular ordering in CuAu alloy is shown to form previous to the horizontal ordering [11], which is also revealed by the time-dependent Landau theory [12] and the molecules dynamics [13], indicating that the evolution times of the two kinetic processes, surface segregation and ordering, are different. The kinetics of the system with the competition of the multi-kinetic processes can result in metastable and transient states [14–17].

In this paper, we study the kinetic process of ordering in a thin film of fcc alloy. We find a phenomenon caused by the confinement of surfaces. The simulations show that the kinetic path of ordering is randomized for the alloy films with weak surface segregation. The same initial structure will relax to the two states with a probability due to the surface confinement.

### 2. Method

We consider an fcc thin film of binary alloy in the (001) direction. We describe the system by the Ising model with the Hamiltonian [18]

$$\mathcal{H} = J \sum_{ij} \sigma_i \sigma_j + \alpha J \sum_{mn} \sigma_m \sigma_n - h_1 \sum_{k \in \{1\}} \sigma_k - h_2 \sum_{k \in \{N\}} \sigma_k \quad (1)$$

where  $J$  is the interchange energy of the nearest-neighbor,  $\alpha$  is the ratio between the next nearest-neighbor and nearest-neighbor interaction energy. In this work, we only consider the nearest-neighbor and the next-nearest-neighbor interactions. The first sum runs over all the nearest neighbor sites and the second sum runs over all the next nearest-neighbor sites. The variable  $\sigma_i = 1$  if the site  $i$  is occupied by the  $A$  species and is  $-1$  otherwise. The energy parameters  $h_i$  represent the SC fields [19]. It describes the effects of confinement on the surface segregated atoms. The last two sums are restricted to the surface layers (layer 1 and layer  $N$ ) on which the SC fields  $h_i$  act. We only consider anti-ferromagnetic nearest-neighbor and ferromagnetic next nearest-neighbor interactions, i.e.  $J > 0$  and  $\alpha < 0$ , which corresponds to an alloy system with  $L1_0$  and  $L1_2$  bulk structures, of which the kinetic processes are extensively studied [20,21]. In this work, the values of energy parameters are normalized with  $J$ .

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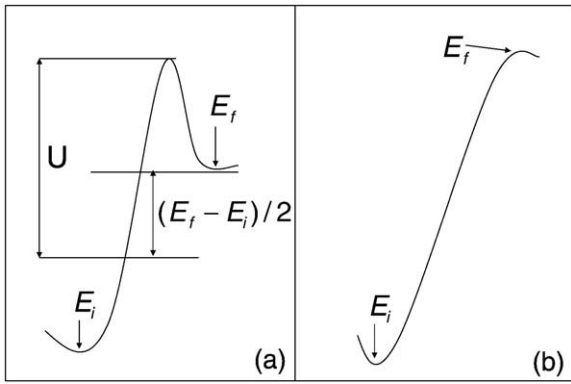


Fig. 1. A sketch of the energy curve for atomic exchange.  $E_i$  and  $E_f$  are the energies before and after exchange, respectively.  $U$  is defined as the activation energy. (a) The case of  $\Delta E = E_f - E_i < 2U$ ; (b) the case of  $\Delta E > 2U$ .

In order to simulate the kinetics of alloys, we use Kawasaki dynamics in our Monte Carlo (MC) simulations [22,23] and consider the atomic exchanges between nearest-neighbors with the atomic activation energy  $U$ . As shown in Fig. 1(a), usually, there is a barrier for atoms exchange with their nearest neighbors. The activation energy  $U$  is defined as the energy difference between the peak and the midpoint of before and after exchange. In our simulation, we assume that  $U$  is constant for all atomic exchanges. So that, the acceptance probability of each random exchange attempt is defined as  $P = \exp(-U/k_B T - \Delta E/2k_B T)$ , where  $\Delta E = E_f - E_i$  is the energy difference after and before exchange. However, in the case that  $U < |\Delta E|/2$ , the energy curve would be of the type of Fig. 1(b), the acceptance probability is correspondingly changed to Metropolis type  $P = \exp(-\Delta E/k_B T)$ . It is easy to prove that this mechanism satisfies the detailed balance condition. In one MC step, every site has undergone one exchange attempt averagely. We simulate the kinetics mainly on a  $16 \times 16 \times N$  sample with periodic boundary conditions. Our simulations on larger samples such as  $32 \times 32 \times N$ ,  $64 \times 64 \times N$  and  $128 \times 128 \times N$  show the similar results.

To calculate the order parameters, the square lattice of each plane of the film is divided into two sublattices:  $\alpha$  and  $\beta$ . The long range order parameter of the  $i$ th plane is defined as  $\eta_i = |n_{\alpha_i}^A - n_{\beta_i}^A|/N$ , where  $N$  is the site number of each sublattice and  $n_{\alpha_i}^j$  is the number of  $j$  atomic species in the  $\alpha$  sublattice of the  $i$ th plane. In this way, the states of the system can be described as  $\eta_1 \eta_2 \dots \eta_N$ . To simulate a quench from high temperature to a temperature below  $T_c$ , we take the disordered state as the initial state of the system. To study the effects of initial fluctuations to the final states, we have used different disordered initial states, which will be discussed in detail below.

### 3. Results and discussion

We consider the kinetic processes of  $AB_3$  films with even layer number. Ground state studies [24] show that in the structures of ground states, there are two kinds of layers: i) the layer occupied purely by  $A(B)$  atoms (denoted as  $A(B)$ ). ii) the layer that contains equal numbers of  $A$  and  $B$  atoms (denoted as  $C$ ). When  $h/J > -0.4$  for the symmetric SC field ( $h_1 = h_2 = h$ ) and  $\alpha = -0.2$ , the ground state of the film with six layers is  $L1_2$  like  $(CBCBCB)$  (or symmetrically  $(BCBCBC)$ ) (Fig. 2(a)), which is denoted as  $O$  state. When  $h/J < -0.4$ , the ground state is  $(BCBCCB)$  (Fig. 2(b)), which is denoted as  $O'$  state, i.e. the  $O$  state with truncated bulk structure is the ground state for the weak SC field, while the  $O'$  state is the ground state corresponding to the strong SC field. For the films with odd layer number, there is only the truncated bulk state  $O$ . Since  $O$  and  $O'$  states correspond to the case of strong bulk ordering and that of strong surface confinement respectively,

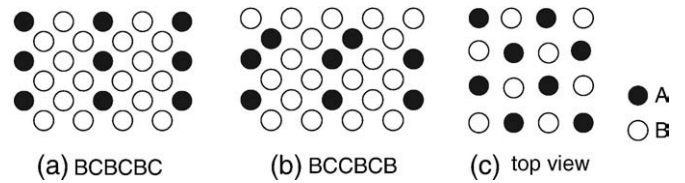


Fig. 2. Structures of  $(BCBCBC)$  and  $(BCBCCB)$  in six-layer films. (a) Side view of  $(BCBCBC)$  structure. (b) Side view of  $(BCBCCB)$  structure. (c) Top view of C layer.

the kinetics of ordering to these two states shows the features related to the competition between surface confinement and ordering.

For  $AB_3$  six-layer films, we find that the kinetic path of ordering is randomized when SC field is weak. The simulations are repeated for 800 times with randomly disordered initial structures. According to MC simulations, the critical temperature of order-disorder transition of this system is  $T_c = 4.2J/k_B$  when  $h/J = -0.3$ . When  $1.4J < k_B T < 4.2J$ , the stable state of the system is a symmetric partially ordered state of type  $O'$ . When  $k_B T < 1.4J$ , the stable state changes to the ordered  $O$  state. Thus when  $k_B T/J < 1.4$ , the final state should be  $O(CBCBCB)$ . In our simulation, we found that the kinetic process shows two stage evolutions. In the first stage, the system reaches the stable state  $O(CBCBCB)$  and the metastable state  $O'(BCBCCB)$  with a probability. The probability that system reaches  $O$  state is affected by the environment. In the second stage, the metastable state gradually evolves to the stable state. In the following, we first study the kinetic process of the first stage.

Fig. 3(a) shows the probability  $P_O$  under different SC field  $h$  and temperature.  $P_O$  is defined as the ratio of the times that the films reach the stable  $O$  state to the total times of repetitions. The values are taken at 65000 MC steps. As  $h$  increases from  $-0.5J$  to  $-0.2J$ ,  $P_O$  increases from 0 to 1. We have made the comparison of data for the samples with various sizes.  $P_O$  for the samples with sizes up to  $128 \times 128 \times 6$  is

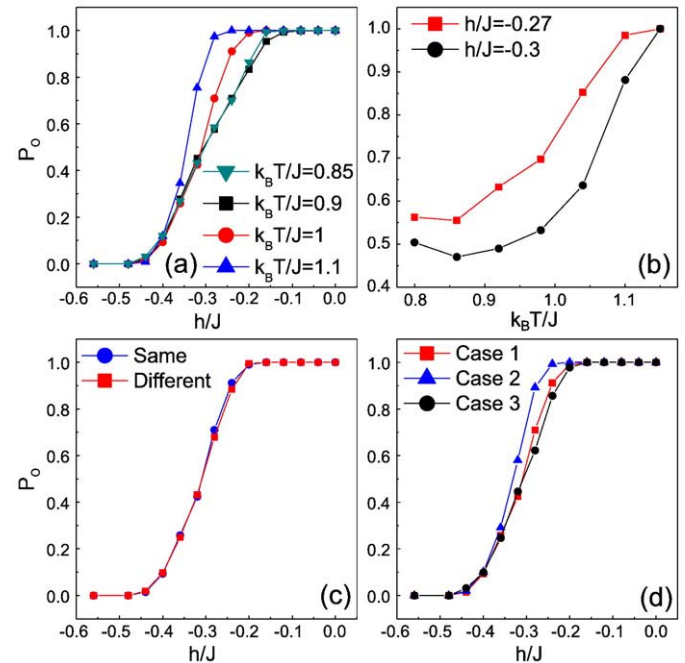


Fig. 3. (a) The probability  $P_O$  as a function of confinement field. (b) The probability  $P_O$  as a function of temperature. All samples are started with random disordered initial structures. (c) The probability  $P_O$  starting with the same disordered initial structure or different disordered initial structures. (d) The probability  $P_O$  as a function of SC field with different types of initial fluctuations. Case 1 is for the random replacement. Case 2 is for the symmetric fluctuations. Case 3 is for the asymmetric fluctuations.  $U/J = 1.8$  and  $\alpha = -0.2$ .

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