

Growth Kinetics in a Lattice-Gas Model with Anisotropic Jump Probabilities

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The growth of the $p(2 \times 2)$ domains in the lattice-gas model with anisotropic probabilities of atomic jumps has been investigated using the Monte Carlo simulation. The analytical approach as well as the simulation results suggest that this model exhibits the anomalously slow growth of a characteristic domain size $R(t) \propto t^{1/5}$ instead of $R(t) \propto t^{1/3}$ for the jump-isotropic model. The growth rate as a function of the atomic concentration has a pronounced maximum at a concentration well below the stoichiometric concentration of the $p(2 \times 2)$ phase.

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The growth of ordered domains in a system exhibiting phase transition at a temperature T_c for the case of rapid quench from $T > T_c$ to $T < T_c$ is a very interesting and important problem (see [1,2] and references therein). It has been predicted that growth kinetics may exhibit a self-similar temporal behavior with a single characteristic length $R(t)$ associated with the average domain or island size. Therefore it should undergo to universal scaling laws depending on the universality class of the system only [3].

Analytical approaches to the growth problems are usually based on the idea of domain walls (or island boundaries) motion. A force acting on the wall is assumed to be proportional to its curvature. In this way the following equation:

$$\dot{R} \approx C/R^2 \quad (1)$$

is obtained for the Ising model with the conserved scalar order parameter. First used by Lifshitz [4,5], these ideas have been further developed by Huse [6], and lead to the relation

$$R(t) = Bt^{1/3} + A. \quad (2)$$

For the coefficient B the theory gives $B \approx \chi D \Sigma$, where χ is the susceptibility of the system, D is the chemical diffusion coefficient, and Σ is the domain wall energy per unit length. The second term A in the right-hand side of Eq. (2) arises due to the interaction between neighboring domains. Monte Carlo simulations performed up to now have confirmed the growth law (2) for the classical Ising model [7] as well as for some other systems with a more complex (*vector*) order parameter (e.g., [8]).

In real physical systems the interatomic interaction is not reduced to the interaction of nearest neighbors only. In submonolayer films adsorbed on crystal surfaces the interaction may be anisotropic, and it may oscillate with interatomic distance [9]. Ala-Nissilä *et al.* [10] demonstrated that the anisotropy of interactions results in the anisotropy of growing domains. It is evident, however, that anisotropic systems should be characterized not only by the interaction anisotropy, but also by the

anisotropy of probabilities of atomic jumps in different directions. The jump anisotropy does not modify the thermal equilibrium state of the system, but it must modify the kinetics of phase transitions.

In the present work we investigate the extreme case of the jump-anisotropic model, namely the model where atomic jumps are allowed in a single direction only. Such a generalization may not essentially modify the growth kinetics for the standard Ising model, which should still obey Eq. (2) with smaller coefficients A and B . The situation, however, must be drastically changed for a more complicated lattice-gas model where the ordered phase corresponds to a degenerated rarefied structure.

We study the lattice-gas model with a fixed atomic concentration characterized by the "coverage" $\theta = \mathcal{N}/\mathcal{M}$, where \mathcal{N} is the number of atoms and \mathcal{M} is the number of the lattice sites. We take into account atomic interactions up to third neighbors with the energies $\varepsilon_1, \varepsilon_2$, and ε_3 for the nearest, next-nearest, and third neighbors, respectively, and assume a *repulsion* of nearest and next-nearest neighbors and an *attraction* of third neighbors. For such a choice of interactions the low-coverage ordered phase for $\theta \leq \frac{1}{4}$ corresponds to the $p(2 \times 2)$ structure, and with decreasing of temperature the system is to exhibit the first-order phase transition to this phase. Below we restrict our analysis to the low-coverage region $\theta \leq \frac{1}{4}$ only.

The $p(2 \times 2)$ structure is fourfold degenerate, so one may recognize four sublattices denoted as X_1, X_2, Y_1 , and Y_2 . The main aspect of the model under consideration is that the atoms are allowed to jump for one lattice constant in the x direction only. As a result, X_1 domains can be transformed into X_2 domains (as well as Y_1 into Y_2), but the transformation of the X -type domains into the Y -type ones is forbidden. Thus, four types of domains are split into two classes X and Y .

The jump-anisotropic model exhibits two different types of domain walls. The first type corresponds to the $X_1|X_2$ (or $Y_1|Y_2$) walls which can be shifted by a jump of a single atom for one lattice constant in the x direction. Consequently, the dynamics of these walls has to be described by the law (2). During a short time the walls

of the first type have to disappear (if two domains of, e.g., the X_1 and X_2 types come into contact, a larger domain has to devour the smaller one). Thus, the first growth stage has to finish with a configuration where the X -type domains are surrounded by the atoms belonging to the Y sublattice, so that only boundaries between the X and Y types of domains remain.

The second type of domain walls is the $X|Y$ wall. In the jump-anisotropic model the $X|Y$ wall cannot be shifted by an ordinary mechanism of a single atomic jump. To shift the $X|Y$ wall, an atom of, say, the X domain must cross the area occupied by the Y domain and then join any other X domain. To estimate the rate of this process, recall that in the jump-isotropic model the elementary act of the domain wall motion is a jump of an atom in the domain wall region for one lattice constant, so the prefactor C in Eq. (1) is proportional to τ^{-1} , where τ is the mean time between consequent atomic jumps. In the jump-anisotropic model, however, an "elementary act" has to be an atom crossing a distance R over the alien structure. This process will take a time of the order $\tilde{\tau} \sim R^2/D^*$, where D^* is the diffusion coefficient over the alien structure. Putting $C \propto \tilde{\tau}^{-1}$ into Eq. (1), we obtain the relation $\dot{R} \propto R^{-4}$ which leads to the growth law

$$R(t) = Bt^{1/5} + A. \quad (3)$$

Thus, the jump-anisotropic model is characterized by two-stage hierarchy of growth rates, and the late stage is described by the slow growth law (3). Because of the anisotropy of the model, the coefficients in Eq. (3) for island sizes in the x and y directions are different so that an island shape has to be anisotropic in a general case.

In Monte Carlo (MC) simulation we have studied the 60×60 square lattice with periodic boundary conditions. As initial configuration we took a random distribution of atoms, and then the system was allowed to evolve according to the standard Metropolis algorithm. For the interaction energies we have taken $\varepsilon_1 = \varepsilon_2 = -\varepsilon_3 = 1$ and the temperature has been chosen as $T = 1/3$. This temperature is expected to be lower than the melting temperature T_c for the $p(2 \times 2)$ phase (recall that the standard Ising model has $T_c \approx 0.567$). Simulations have been performed for Monte Carlo time t_{\max} .

We calculated the number of islands (domains) of the $p(2 \times 2)$ structure, the number of atoms in each island, and the average island sizes in the x and y directions. To find the number of atoms in a given island, we used the direct method which is based on the cluster labeling technique widely used in percolation problems [11]. Namely, we looked for the atoms which have no nearest and no next-nearest neighbors. To avoid the influence of the percolation, we assume that a given atom belongs to the given island if this atom has at least two cross-situated third neighbors. Then we calculated the number of atoms $N^{(i)}$ in the given i th island as well as

the average number of atoms $R_x^{(i)}$ and $R_y^{(i)}$ along the x and y axes, respectively, by scanning the island along these axes. At the same time we calculated the total number of islands N_{isl} . The mean island sizes N , R_x , and R_y were determined by the relations [12]

$$N = \frac{\sum_{s=1}^{\infty} s^2 n(s)}{\sum_{s=1}^{\infty} s n(s)}, \quad R_x = \frac{\sum_{s=1}^{\infty} s^2 n_x(s)}{\sum_{s=1}^{\infty} s n_x(s)}, \quad (4)$$

where $n(s)$ and $n_x(s)$ is the number of islands containing s atoms either in total or along the x direction, respectively. Finally, the results were averaged over runs; we have made 10^2 runs for $t_{\max} = 10^4$, 10 runs for $t_{\max} = 10^5$, and only one run for $t_{\max} = 10^6$ MC steps per atom. The obtained time dependences are compared with those for the model with equal jump probabilities in all directions which have been calculated for the same energy parameters. Besides, we have also calculated the total number of atoms within the ordered phase defined as

$$\mathcal{N}_{\text{tot}} = N_{\text{isl}} N. \quad (5)$$

Time dependences for the mean island sizes N , R_x , and R_y are shown in Fig. 1. We also have plotted the least square fits of the \sqrt{N} , R_x , and R_y versus time using the formula (3). As one can see, the simulation results are in good agreement with theoretical predictions [13].

In some physical systems, especially in layers adsorbed on crystal surfaces, the atomic concentration may vary within a wide range, so the question arises about the concentration dependence of the growth rate. For the lattice-gas model with the attraction of nearest neighbors only, according to Huse's theory [6] the coefficient B is proportional to the susceptibility χ which, on the other hand, is proportional to θ . Thus, $B(\theta) \propto \theta$. For

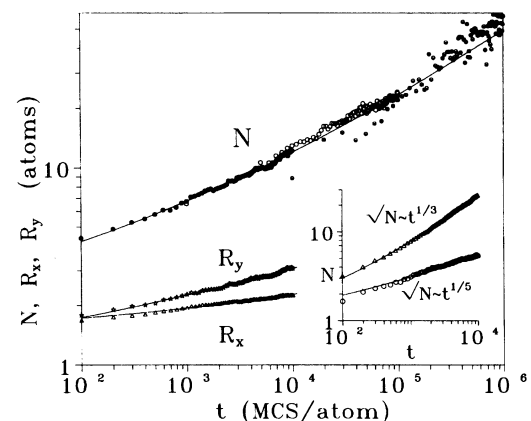


FIG. 1. Average sizes N , R_x , and R_y of a $p(2 \times 2)$ island versus time for the jump-anisotropic model at $\theta = 0.1875$. Solid curves are the best fits (3) for \sqrt{N} , R_x , and R_y . Inset: comparison of $N(t)$ dependences at $\theta \approx 0.03$ for jump-isotropic (triangles) and jump-anisotropic (circles) models; solid curves are the best fits (2) and (3), respectively.

the jump-anisotropic model at small θ , $\theta \ll \theta_0 = 1/4$, growing islands are situated far from one another, and grow independently. Therefore it is expected that the coefficient B in Eq. (3) is to be proportional to θ too, $B(\theta) \propto \theta$ at $\theta \ll \theta_0$. On the other hand, at higher coverages, $\theta \sim \theta_0$, neighboring islands which belong to the different classes X and Y start to overlap. The overlapping results in the decrease of the growth rate, because an island of, say, the X type will impede the growth of a neighboring island of the Y type. Thus, there is a concentration θ_* such that $B(\theta) \propto \theta$ for $\theta < \theta_*$ but $B(\theta)$ decreases with θ in the interval $\theta_* < \theta < \theta_0$, i.e., $B(\theta)$ has to have a maximum at $\theta \sim \theta_*$. Since the value θ_* corresponds to the situation when islands start to overlap for the first time, θ_* is to be coupled with the percolation threshold (which is ~ 0.5 for square lattices). So we obtain $\theta_* \sim 0.5\theta_0 = 1/8$. The simulation results presented in Fig. 2 confirm these qualitative considerations.

Now let us consider the concentration dependence of the number of islands on a given area, $N_{\text{isl}}(\theta, t)$. $N_{\text{isl}}(\theta, t)$ can be represented in a form $N_{\text{isl}}(\theta, t) = \mathcal{N}P(\theta, t)$, where the function $P(\theta, t)$ depends on θ . Besides, we can also write $P(\theta, t) = \sum_s P_s(\theta, t)$, where $P_s(\theta, t)$ is the probability of finding an island consisting of s atoms. At $t = 0$, when the atomic configuration is random, the probability of finding an "island" consisting of a single atom is equal to the probability of finding an atom surrounded by eight empty lattice sites, so that $P_1(\theta, 0) = \theta(1 - \theta)^8$. Next, we may take approximately $P_s(\theta, 0) \approx P_1^s(\theta, 0)$. Because $\mathcal{N} = \theta \mathcal{M}$ and \mathcal{M} is fixed, we finally obtain $N_{\text{isl}}(\theta, 0) \propto \theta^2(1 - \theta)^8$. This function has a maximum at $\theta = 0.2 < \theta_0$. The results of simulations show that the shape of the function $N_{\text{isl}}(\theta, t)$ does not change essentially at least up to the time 10^4 MC steps per atom.

Now we can predict the concentration dependence for the total number of atoms in the ordered phase $\mathcal{N}_{\text{tot}} = N_{\text{isl}}N$. Combining the results obtained above, we see

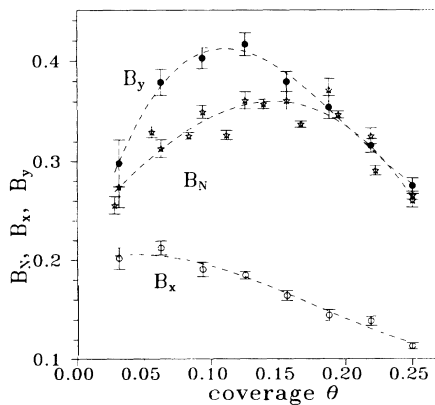


FIG. 2. Coverage dependences of the prefactors B_N , B_x , and B_y [Eq. (3)] for the jump-anisotropic model.

that \mathcal{N}_{tot} as a function of θ should have a maximum at $\theta \sim 0.5\theta_0$. This maximum is more pronounced if we consider the relative rate of island growth, defined as

$$H(\theta) = \mathcal{N}_{\text{tot}}(\theta)/\mathcal{N}. \quad (6)$$

Thus, in the jump-anisotropic model the most effective growth of islands of the ordered $p(2 \times 2)$ phase takes place at atomic concentration $\theta \sim 0.5\theta_0$, i.e., at the concentration much lower than the commensurate one (see Fig. 3). Notice that the atomic configuration at $\theta \approx 0.5\theta_0 = 1/8$ consists of isolated slowly growing islands separated by the disordered "lattice-gas" phase. This situation is different from that for the jump-isotropic model, where, *first*, islands must grow much faster, *second*, the maximum growth rate $H(\theta)$ occurs at $\theta = \theta_0 = 1/4$ (Fig. 3), and, *third*, the resulting configuration should correspond to compact continuous phase.

Now let us discuss the applicability of the described model to surface diffusion combined with phase transitions. If we prepare an initial state where atoms randomly occupy half of the surface only (for $x \leq 0$) with a coverage θ_{ini} , the step in the coverage will smooth as the time increases, and a phase transition occurring at $\theta = \theta_0 < \theta_{\text{ini}}$ may manifest itself in the shape of the coverage tail $\theta(x)$ at $x > 0$. At the first-order phase transitions the chemical diffusion coefficient D falls to zero [14], because at the transition point the equilibrium state corresponds to coexistence of two phases. As a result the tail shape $\theta(x)$ should exhibit a sharp drop at x^* from the ordered phase coverage θ_0 at $x < x^*$ to the value θ_g at $x > x^*$ where θ_g ($\theta_g < \theta_0$) corresponds to the lattice-gas phase. We emphasize, however, that the tail function $\theta(x)$ monotonically decreases with x .

For the jump-anisotropic model the situation, however, is different. Actually, because the rate of island growth has a maximum at $\theta \approx 0.5\theta_0$, the growth of islands

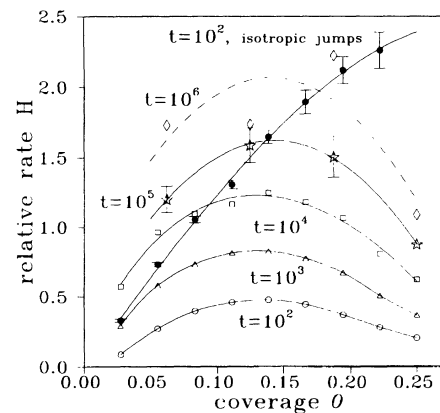


FIG. 3. Relative rate (6) of the $p(2 \times 2)$ islands growth versus coverage at different MC times for the jump-anisotropic model: 10^2 (open circles), 10^3 (triangles), 10^4 (squares), 10^5 (stars), and 10^6 (rhombs) MC steps per atom. Similar quantity for the jump-isotropic model is shown by filled circles.

of the ordered phase will proceed most effectively at distances x^* where the tail concentration $\theta(x^*)$ is about $\theta_* \sim 0.5\theta_0$, while the growing islands should correspond to the concentration θ_0 . As a result the tail function $\theta(x)$ might become nonmonotonic, and a "hollow" would appear at distances x^* . Such a peculiarity has in fact been observed in experiment [15] performed for lithium atoms adsorbed on the furrowed (112) plane of molybdenum, where the diffusion in the $[\bar{1}\bar{1}1]$ direction (along the furrows) has been studied. The initial step was taken to be $\theta_{\text{ini}} \approx 0.04$. Two remarkable features were noticed in the diffusion tail $\theta(x)$: *first*, the formation of the extended plateau $\theta'_0 \approx 0.015$, *second* the shaping of the clear-cut hollow immediately behind the spreading plateau with the concentration $\theta' \sim 0.5\theta'_0$ (for details see [15]).

If the theory developed in the present work could be applied to the experiment [15], the plateau would have a structure of θ_0 islands separated by the lattice-gas phase. The ordered phase should correspond to a long-period rarefied structure of a $p(m \times m')$ type with $m \sim m' \sim 7$, i.e., the adatoms have to attract each other at distances $r \sim 7a_{\text{lattice}}$ but repel at smaller distances. Such an interaction can really exist due to the competition between the dipole-dipole repulsive and the long-range oscillating indirect interaction of adatoms [9]. Low energy electron diffraction (LEED) experiments for the Li-Mo(112) adsystem (as well as for a number of other adlayers on the anisotropic surfaces [9]) showed that along the furrows the interaction is oscillating and may exhibit a local minimum at the distances $r \sim 7a_{\text{lattice}}$. So it may be supposed that a similar oscillating interaction may also exist in the direction across the furrows. Unfortunately, there are no reliable LEED experiments at coverages $\theta < 0.1$. Moreover, according to the results of the present work, it is too conjectural to prepare the ordered rare phase in the strictly anisotropic system because its growth kinetics would be extremely slow. However, the rarefied phase in the diffusional tail may be observed by the scanning tunnel microscope technique.

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